

K-BENTONITES OF THE ORDOVICIAN DECORAH SUBGROUP, UPPER MISSISSIPPI VALLEY: CORRELATION BY CHEMICAL FINGERPRINTING

Dennis R. Kolata Joyce K. Frost Warren D. Huff



Cover photo: Outcrop near Dickeyville, Wisconsin (locality 40), showing typical stratigraphic relationships of the Decorah Subgroup. The Deicke and Millbrig K-bentonite Beds occur in the basal part of the Spechts Ferry Shale Formation (near upper 40 cm of the meter stick—bottom center). The Elkport and Dickeyville K-bentonite Beds occur in the Guttenberg Limestone Formation in the upper part of the outcrop.

Graphic artists: Jacquelyn Hannah and Lauren Toolson

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K-BENTONITES OF THE ORDOVICIAN DECORAH SUBGROUP, UPPER MISSISSIPPI VALLEY: CORRELATION BY CHEMICAL FINGERPRINTING

ABSTRACT

Widely distributed outcrops and cores of the Champlainian (middle Ordovician) Decorah Subgroup in the Mississippi Valley region have been correlated on the basis of the chemical composition of K-bentonite beds. The K-bentonites were analyzed for 26 elements by either instrumental neutron activation or X-ray fluorescence methods, and the data were treated by stepwise discriminant analysis. The elements that serve as the best discriminators of chemical composition between beds are (in order of atomic number) Na, Sc, Ti, Zr, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, and Th. These are the elements that have different average concentrations from bed to bed, but relatively small ranges of concentration within beds.

The Deicke, Millbrig, Elkport, and Dickeyville K-bentonite Beds of the Decorah Subgroup each have unique chemical fingerprints that probably reflect differences in the original composition of the parent volcanic ash. The distinctive chemical signatures of the Deicke and Millbrig have been measured in outcrop and subsurface samples between southeastern Minnesota and southeastern Missouri, a distance of about 900 km. The Deicke has also been chemically identified in the subsurface of northwestern Iowa. Isopach maps indicate that both beds thicken toward the southeast. The Elkport and Dickeyville are chemically identifiable only in the northern outcrop area of the Mississippi Valley. Two K-bentonite beds occur in places above the Millbrig K-bentonite in the Kings Lake Formation in eastern Missouri, but the chemical data are too inconclusive to assign them to any formally named beds.

The House Springs K-bentonite Bed (new), a chemically distinct and widespread unit up to 3 cm thick, occurs in the basal Dunleith Formation approximately 1 m above the Kings Lake Formation in eastern Missouri.

The K-bentonite correlations indicate that some Decorah formations and members are laterally gradational, whereas others are uniform in thickness and lithology over wide areas.

INTRODUCTION

Ordovician K-bentonites (altered volcanic ash beds) occur in outcrop and subsurface over approximately 1.3 million square km (500,000 square miles) of eastern North America (fig. 1). They are distributed through a thick succession of carbonates and terrigenous clastics that are characterized by complex facies relationships. The ash probably originated from volcanoes situated in an island arc system in the Appalachian mobile belt because the K-bentonite beds are more numerous, thicker, and coarser in, or adjacent to, the Appalachians than in areas farther west. Paleowinds from the east-northeast (in terms of present geographic coordinates) apparently carried the ash over the Midcontinent, where it fell into widespread epeiric seas.

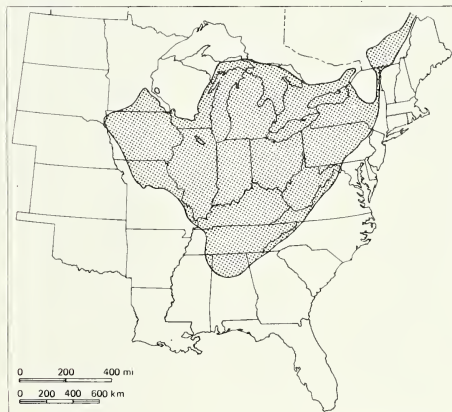


Figure 1. Distribution of Ordovician K-bentonite beds (shaded area) in the eastern United States and Canada.

- the occurrence of numerous K-bentonite beds in certain regions—30 different beds were reported by Kay (1935) in the Champlainian (middle Ordovician) rocks near Strasburg, Virginia;

- the mineralogical similarity of different beds over wide areas; and
- the suspected lack of continuity of individual beds from one region to another (i.e., some beds show evidence of reworking, which suggests that others may have been destroyed).

Recently, Ordovician (Blackriveran and Rocklandian) K-bentonites in Ohio, Kentucky, and Tennessee have been correlated using methods based on differences in chemical composition (Huff, 1983). Huff's methods were similar to those in reports on correlation using chemical fingerprinting of volcanic ash layers in the western United States (Randle et al., 1971; Borchardt et al., 1971; Borchardt et al., 1973; Smith and Nash, 1976), and in reports on the use of minor and trace elements to distinguish volcanic rocks from

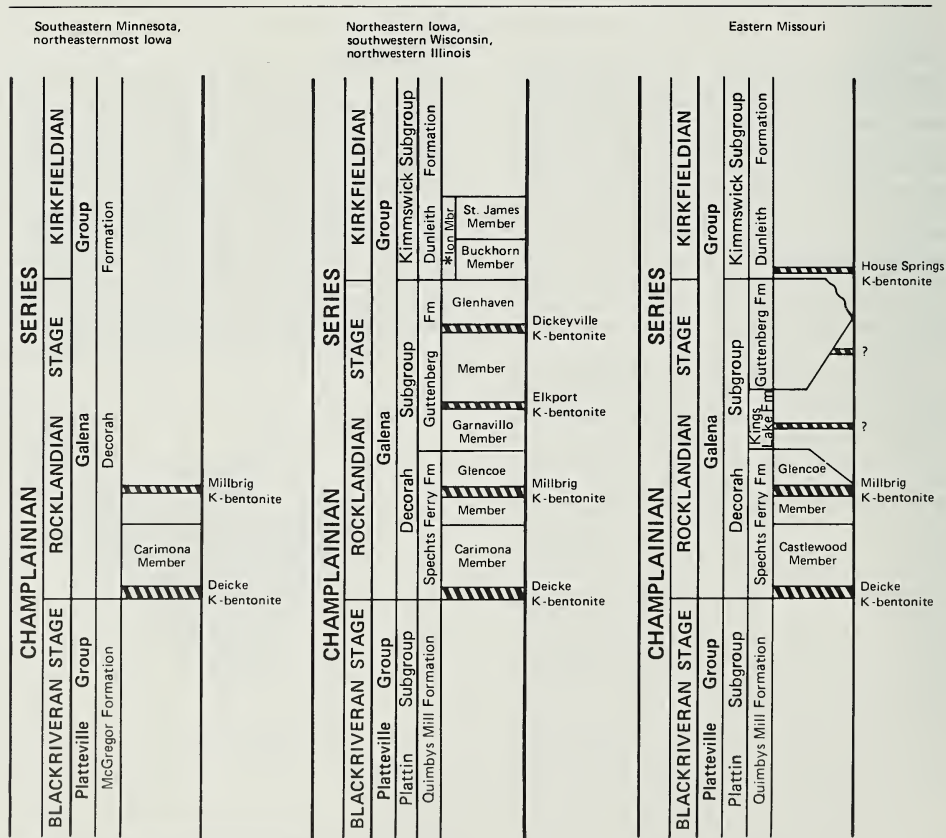


Figure 2. Classification of the Decorah rocks in the Upper Mississippi Valley region. The Ion Member of the Dunleith Formation is restricted to northeastern Iowa.

different sources (Jack and Carmichael, 1969; Pearce and Cann, 1973; Pearce, 1975; Winchester and Floyd, 1977; Wood et al., 1979). In this report we have expanded upon the methods of Huff (1983) to chemically correlate different K-bentonites in the Rocklandian Decorah Subgroup of the Upper Mississippi Valley (the area drained by the Mississippi River north of its confluence with the Ohio River).

At least 18 K-bentonite beds from Ordovician rocks of the Upper Mississippi Valley are known; 15 occur in the Champlainian and Cincinnati Galena Group. This study concentrates on the Deicke, Millbrig, Elkport, and Dickeyville K-bentonite Beds (Willman and Kolata, 1978) of the Decorah Subgroup, Galena Group (fig. 2). Also included are several K-bentonite and K-feldspar beds situated above the Millbrig in the Decorah of eastern Missouri. The data are based primarily on samples collected in outcrops between St. Paul, Minnesota, and Cape Girardeau, Missouri, a distance of approximately 900 km (fig. 3). Most of the localities are in southeastern Minnesota, northeastern Iowa, southwestern Wisconsin, northwestern Illinois, and eastern Missouri. A small number of subsurface samples were obtained from cores.

PREVIOUS INVESTIGATIONS

The first descriptions of a K-bentonite bed in the Decorah strata of the Mississippi Valley were made by Sardeson (1924, 1926a, 1926b, and 1927). He described a 2.5 to 15 cm bed near the base of the Decorah in parts of Wisconsin and Minnesota. He assumed that it was the same bed that Nelson (1922) had described in Tennessee. It is clear from Sardeson's stratigraphic description that he was observing the Deicke K-bentonite Bed. He later (1928, 1934) described another K-bentonite, now known to be the Millbrig K-bentonite Bed, in the Decorah shale at Minneapolis, Minnesota. Subsequent stratigraphic studies of the Decorah K-bentonites include those by Kay (1931, 1935), Allen (1932), Herbert (1949), Bell (1954), Weiss and Bell (1956), Templeton and Willman (1963), and Willman and Kolata (1978).

Allen (1929) provided the first mineralogic description of the Decorah K-bentonites. The pyroclastic origin was shown by the presence of sanidine, hornblende, biotite, and euhedral zircon and apatite. Additional mineralogic and stratigraphic information was published by Mossler and Hayes (1966). They did not believe that regional correlations of Ordovician K-bentonites were feasible at that time.

STRATIGRAPHIC FRAMEWORK OF THE DECORAH SUBGROUP

The Decorah Subgroup (Templeton and Willman, 1963; Willman and Kolata, 1978) composes the lower part of the Galena Group in the Mississippi Valley (fig. 2). It is assigned to the Rocklandian Stage of the Champlainian Series primarily on the basis of conodonts (Branson and



Figure 3. Index map of the Upper Mississippi Valley region showing the distribution (shaded area) of Decorah rocks at the bedrock surface.

Mehl, 1933; Stauffer, 1935; Webers, 1966; Sweet and Bergstrom, 1976; Sweet, 1984). The Decorah occurs at the bedrock surface in two major areas of the Mississippi Valley (fig. 3): (1) a northern V-shaped area, one limb of which extends from north-central Illinois through eastern Wisconsin, and the other along the Mississippi River valley up to St. Paul, Minnesota. Exposures of the Decorah are more numerous along the western limb. (2) a southern area with exposures occurring between New London, Missouri, and Batchtown, Illinois, and in the Missouri and Mississippi River valleys on the north and east flank of the Ozark Dome. The Decorah occurs in the subsurface between the northern and southern areas.

The Decorah consists of shale and shaly carbonate formations that include (in ascending order) the Spechts Ferry, Kings Lake, and Guttenberg Formations (fig. 2). Along a northeast trending line approximately from Calmar to Lansing, Iowa (fig. 3), limestone in the Guttenberg grades northward to greenish gray shale, as it does in the basal part of the overlying Dunleith Formation. Northwest of this line, the Decorah-Dunleith boundary is a diachronous facies transition marked by a gradual increase in shale in the basal part of the Dunleith. Because the Decorah formations lose their identity in this area, it is neither practical nor useful to extend the subgroup level of classification into this area; here we assign the basal shaly strata of the Galena to the Decorah Formation.

Using outcrop and subsurface data, Witzke (1983, fig. 5) showed that the Decorah shale is about 20 m thick in northwestern Iowa. It is approximately 24 m thick at St. Paul, Minnesota (Templeton and Willman, 1963). Thickness patterns and clay mineral facies suggest that the source of the shale was the Transcontinental Arch (Parham and Austin, 1969; Witzke, 1980, 1983).

Above the Guttenberg Formation in parts of northeastern Iowa and southwestern Wisconsin are greenish gray shaly strata that Kay (1929) called the Ion Member (fig. 2). The Ion grades southward to carbonate (Buckhorn and St. James Members of the Dunleith Formation), which is only slightly shaly. Northward, where the Guttenberg limestone grades to shale, the Ion is an undifferentiated part of the Decorah Formation.

In south-central Wisconsin and north-central Illinois, the Spechts Ferry Formation pinches out, the Guttenberg thins greatly, and the Decorah Subgroup, represented by the Guttenberg Formation, is only 0.3 to 1.2 m thick or absent.

The Decorah Subgroup extends southward in western Illinois and eastern Missouri, where it is particularly well developed. We have observed it in outcrop as far south as Ilmo, Missouri, where it consists of approximately 2 m of interbedded grayish green shale and very fossiliferous limestone.

Throughout most of the Upper Mississippi Valley the Decorah conformably overlies the carbonates of the Platteville Group, except in north-central Illinois and south-central Wisconsin, where the contact is marked by a prominent hardground at the top of the Quimbys Mill Formation. The Decorah is conformably overlain by the Dunleith Formation, except south of the general vicinity of the Iowa-Missouri state line, where it is disconformably overlain by the coarse skeletal grainstone of the Dunleith Formation (Kimmiswick Subgroup).

Spechts Ferry Formation

The Spechts Ferry (Kay, 1928, 1929, 1935; Herbert, 1949; Agnew et al., 1956; Templeton and Willman, 1963; Willman and Kolata, 1978) is the basal formation of the Decorah Subgroup. It is present in outcrop and subsurface from its northern area of differentiation near Decorah, Iowa, at least as far south as Ste. Genevieve, Missouri. It can be traced in the subsurface into northwestern Iowa, where it merges with undifferentiated shales of the Platteville and Galena Groups (Witzke, 1983). In northwestern Illinois and southwestern Wisconsin the Spechts Ferry pinches out along an irregular feathered edge extending from near Mineral Point, Wisconsin, southward to near Savanna, Illinois.

Two members are recognized in the Spechts Ferry Formation of eastern Missouri and western Illinois: (in ascending order) the Castlewood and Glencoe (Templeton and Willman, 1963; Willman and Kolata, 1978). At its type section near St. Louis, Missouri (Templeton and

Willman, 1963, p. 235), the Castlewood consists of about 2 m of relatively pure limestone that overlies the Platteville Group (Plattin Limestone). It thins very gradually to the north. It is not clear, however, whether the Castlewood extends into the northern outcrop area. At the base of the Castlewood is the Deicke K-bentonite Bed (Willman and Kolata, 1978), which has the same type section as the Castlewood (locality 60). On the basis of stratigraphic position, Willman and Kolata (1978) correlated the Deicke with the widespread and persistent K-bentonite at the base of the Decorah Subgroup in the northern outcrop area (bentonite A of Bell, 1954; 1-1 of Mossler and Hayes, 1966; "Carimona bentonite" of Weiss and Bell, 1956).

In parts of southwestern Wisconsin and northeastern Iowa at approximately the same stratigraphic position as the Castlewood is a thin, discontinuous, argillaceous limestone called the Carimona Limestone Member (Weiss, 1955). It thickens northward to southeastern Minnesota, its type area, where it is generally about 1.5 m thick but in places is as much as 3 m thick (Weiss and Bell, 1956). In this report we restrict the Castlewood to eastern Missouri and western Illinois and the Carimona to the northern outcrop area. In northeastern Iowa, where the Guttenberg Limestone grades northward to shale and the Spechts Ferry Formation is undifferentiated from the overlying shale, the Carimona becomes the basal member of the Decorah Formation (fig. 2).

The dominantly shaly upper part of the Spechts Ferry is assigned to the Glencoe Member. In eastern Missouri the Glencoe thins northward from approximately 2.5 m thick near Barnhart to 1.6 m at the type section near Eureka to 0.25 m at New London. It is absent in the subsurface in parts of western Illinois. At Spechts Ferry, Iowa, nearly all of the type section (2.3 m) of the formation is the Glencoe Member. The Millbrig K-bentonite Bed (bentonite B of Bell, 1954; 1-2 K-bentonite of Mossler and Hayes, 1966; and "Spechts Ferry bentonite" of Weiss and Bell, 1956) occurs in the Glencoe Member. On the basis of stratigraphic position, Willman and Kolata (1978) correlated the Millbrig at its type section near Galena, Illinois (locality 45), with the widespread and persistent K-bentonite in the Glencoe Member of eastern Missouri and western Illinois. The Millbrig is the K-bentonite bed that Kay (1931) correlated with the Hounsfield metabentonite in the Chaumont Formation near Dexter, Jefferson County, New York. It is also the same bed that Allen (1932) correlated in Missouri, Iowa, Wisconsin, and Minnesota.

Kings Lake Formation

The Kings Lake Formation (Herbert, 1949; Templeton and Willman, 1963) occurs above the Spechts Ferry Formation in eastern Missouri and western Illinois. It is approximately 3 to 4 m thick in the area immediately west and southwest of St. Louis. It thins northward to 2 m thick near New London and pinches out in the subsurface northeast of Burlington, Iowa (Herbert, 1949). The Kings Lake con-

tains grayish green and very dusky red shale partings; thus, it appears to be transitional in lithology between the Spechts Ferry and Guttenberg Formations. It probably represents a facies of the upper part of the Glencoe Member of the Spechts Ferry and the basal part of the Guttenberg Formation. Templeton and Willman (1963) recognized two members in the Kings Lake: the Mincke and Tyson. These subdivisions, however, are not used in this study. The Kings Lake contains at least two K-bentonite beds.

Guttenberg Formation

The Guttenberg (Kay, 1928, 1929, 1935; Templeton and Willman, 1963; Willman and Kolata, 1978) is a distinctive carbonate unit that lies above the Spechts Ferry or Kings Lake Formation (fig. 2). It is widely distributed in outcrop and subsurface from near Decorah, Iowa, to just south of Batchtown, Illinois. The Guttenberg is recognizable in the subsurface across the southeastern half of Iowa (Witzke, 1983) and into western Illinois. It is absent in parts of north-central Illinois but present in subsurface from near Sycamore eastward through the Chicago area. South of Batchtown most of the Guttenberg is truncated by the Dunleith Formation.

The Guttenberg is divided into two members (Templeton and Willman, 1963; Willman and Kolata, 1978): the lower Garnaville and the upper and major part of the formation, the Glenhaven. The Glenhaven contains the Elkport K-bentonite Bed at the base and the Dickeyville K-bentonite Bed in the upper part (corresponding respectively to K-bentonites I-3 and I-4 of Mossler and Hayes, 1966). The type section for the Elkport is at Guttenberg, Iowa (locality 27); and that for the Dickeyville is near Dickeyville, Wisconsin (locality 40).

K-bentonite beds

The K-bentonite beds that are known to occur in the Decorah Subgroup include the Deicke, Millbrig, Elkport, and Dickeyville (Willman and Kolata, 1978) and several unnamed beds that occur in places in the Kings Lake Formation of eastern Missouri. Because they are exposed in numerous outcrops over a wide area of the Upper Mississippi Valley, these K-bentonites provide an excellent opportunity to test the stratigraphic usefulness of chemical fingerprinting in correlation on a regional scale. A greater number of samples are available from the Decorah K-bentonite beds than from any other Paleozoic K-bentonites in the Upper Mississippi Valley.

The Decorah K-bentonites are commonly 5 to 10 cm thick and consist primarily of mixed-layer illite/smectite clay—75% illite and 25% smectite (Mossler and Hayes, 1966). Authigenic K-feldspar is also abundant at some localities. The K-bentonites are commonly semi-consolidated and tend to break with hackly fractures when dry. Hand specimens have a characteristic waxy translucence. When wet, the K-bentonite beds are very plastic and tend to slough away. They are typically dark yellowish orange

(10 YR 6/6) to very pale orange (10 YR 8/2). Where weathering has been minimal, however, as in cores and many new outcrops, they are medium gray (N5). Because the K-bentonites are much less resistant to weathering than the enclosing carbonate-rich rocks, they commonly are marked by a prominent re-entrant on the face of many outcrops (fig. 4).

CHEMICAL METHODS

One hundred and twenty-six whole rock K-bentonite samples from 63 outcrops and 4 cores were chemically analyzed. The sample localities are shown in figures 5 and 6 and listed in appendix 1. Great care was taken to avoid contamination of the samples during collection and laboratory preparation. Samples of doubtful origin or purity were examined by X-ray diffraction analysis to determine their mineralogy. Samples of the freshest possible material were dried, pulverized, and sieved following the methods of Huff (1983). They were analyzed for Na, K, Sc, Cr, Mn, Fe, Co, Zn, Ga, As, Rb, Sb, Cs, La, Ce, Sm, Eu, Tb, Dy, Yb,

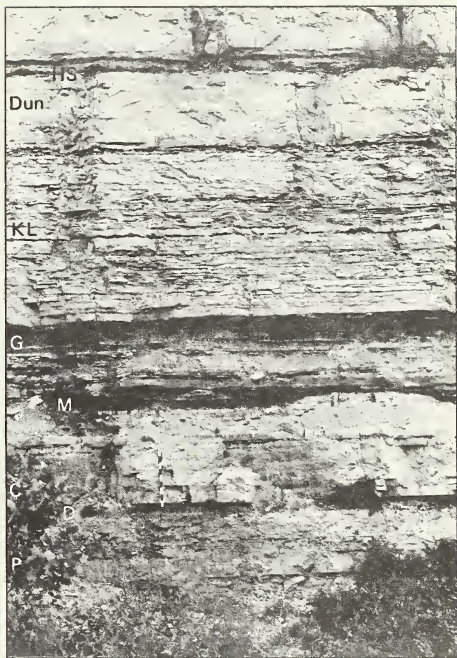


Figure 4. Exposure of the Decorah Subgroup near House Springs, Missouri (locality 62). P, Platteville Group; D, Deicke K-bentonite Bed; C, Castlewood Limestone Member of Spechts Ferry Formation; M, Millbrig K-bentonite Bed; G, Glencoe Shale Member of Spechts Ferry Formation; KL, Kings Lake Formation; Dun, Dunleith Limestone; HS, House Springs K-bentonite Bed. Scale is 1 m.

Lu, Hf, Ta, and Th by instrumental neutron activation analysis (INAA); for Ti by wave-length dispersive X-ray fluorescence spectroscopy (XRF); and for Zr by energy-dispersive X-ray fluorescence spectroscopy (XES).

Instrumental neutron activation analysis of the samples was carried out with thermal neutron irradiation in the Advanced TRIGA reactor at the University of Illinois. The method is comparative: gamma activity of the samples is compared with that of a multielemental standard having a base mixture of spectroscopically pure silica, alumina, and ferric oxide. Aliquots of mixed standard solutions of the analyte elements (other than iron), made from a spectroscopically pure grade of each element or its compound, were pipetted onto the base mixture, which was subsequently dried. Two different irradiations were done. Details of the procedure (the irradiation times, the decay intervals, the count times, the radioisotopes observed, and the principal gamma rays measured) were essentially the same as those outlined for the instrumental neutron activation analysis of shale by Frost, Koszykowski, and Klemm

(1982). Gamma-ray counting was done on either of two high-resolution coaxial Ge(Li) detectors, each connected to a 4096-channel, pulse-height analyzer. Data from each analyzer were recorded on magnetic tape, and the spectra subsequently analyzed by means of a program on the CYBER computer of the University of Illinois. Details of the detector performances and of the rest of the gamma-counting equipment can also be found in Frost, Koszykowski, and Klemm (1982).

The 24 elements determined by INAA in the K-bentonite samples are listed in table 1 with the limits of detection stated for the method as applied. The precision of the elemental determination in the K-bentonites is expressed as the average relative deviation between results on replicates. The values listed apply to most of the results for the K-bentonites. However, when the concentration level was near the detection limit (>1 to 4 times the limit), as was the case for Cr, Mn, Co, Zn, As, and La in some samples, and for antimony in nearly all the samples, a precision of only 40% to 10% relative deviation was obtained.



Figure 5. Map of the northern study area showing sampled localities and lines of cross sections (figs. 14 and 15).

The results obtained on the U.S. Geological Survey (USGS) reference Cody Shale (table 1) also provided information on the accuracy and precision of the determinations of the elements and permit comparison with data obtained by other researchers. Precision of the results for the 24 elements determined by INAA is well within the limits of quantitative determination. The result for gallium is higher and that for cerium is lower than results reported in the literature.

Zirconium was determined on a 1-gram sample (infinite thickness) of K-bentonite powder by XES using a Si(Li) detector with a ^{241}Am excitation source and a tin secondary target. Details of the method were given in Ruch et al. (1979). USGS rock standards were used. Matrix corrections were made by the Compton scatter method after correction for strontium interference. Titanium was

likewise determined by XRF spectroscopy. Results were calculated by linear regression on a curve of peak intensity versus concentration based on data for ten USGS rock standards, after correction for background. As shown by the results on SCo-1 in table 1, zirconium and titanium were both determined with good precision and accuracy.

Fifteen samples that showed chemical anomalies were analyzed for major and minor elements by standard XRF analysis (Ruch et al., 1979). Fourteen high K-feldspar samples were analyzed by XRF for calcium and phosphorus.

STATISTICAL METHODS

A suite of 25 Deicke, 24 Millbrig, 6 Elkport, and 5 Dickeyville samples collected at 39 localities (marked by asterisks in appendix 1 and table 2) in the northern outcrop area where stratigraphic control is very good provided the control group to determine whether each of the four beds carries a unique and identifiable chemical fingerprint. The rest of the Decorah samples consisted mainly of K-bentonites from the southern outcrop area. Their identification was inferred from stratigraphic position. These and several samples from unknown beds were then tested against the results of the discriminant analysis on the control set.

The discriminant analysis was carried out following the method of Huff (1983). A detailed description of the discriminant analysis program can be found in SPSS, Inc. (1984).

For the control group, the concentration of each element by sample and by bed was entered into the computer. In the case of antimony, where the concentration in many samples was below the limit of detection, the "less than" values reported were entered as real values. Basic statistics such as mean and variance were calculated for each element in each bed and correlation analyses were performed on the group. The data for each element were then tested by one-way analysis of variance to determine whether the mean concentrations were different between the beds.

The ratio of the mean between-group (group = K-bentonite bed) variance to the mean within-group variance is the F value. This statistic was used as a basis for ranking the individual elements in decreasing order of apparent discriminating power: Yb, Dy, Sc, Lu, Zr, Na, Ti, Hf, Tb, Eu, Co, Fe, Ta, As, Th, Sb, Sm, Mn, K, La, Rb, Ce, Cs, Ga, Cr, and Zn.

We evaluated this list for elements that were not likely to represent original ash composition. Zinc was apparently randomly distributed, and concentrations of chromium and gallium were not different between beds at the 95% confidence level of significance. Between-bed differences in the concentrations of Cs, Ce, Rb, and La were significant at the 95%, but not at the 99%, confidence level. As discussed in the following section on chemistry of the K-bentonites, the levels of the lightest rare earth elements—lanthanum and cerium—will be most affected in transformation of volcanic ash to K-bentonite. Cesium and rubidium sub-



Figure 6. Map of the southern study area showing sampled localities and line of cross section (fig. 16).

Table 1. Limits of detection and precision of analysis of K-bentonites and SCO-1 (values in ppm unless otherwise noted)

Method	Element	SCO-1		Limit of detection in K-bentonites	Average relative deviation (%)
		This study*	Previous studies†		
INAA	Na ₂ O (%)	0.95 ± 0.02	0.90 ± 0.07	10	5
	K ₂ O (%)	2.78 ± 0.05	2.77 ± 0.08	120	5
	Fe ₂ O ₃ (%)	5.25 ± 0.16	5.14 ± 0.13	700	5
	Sc	13.7 ± 0.4	11 ± 1	0.02	7
	Cr	67 ± 2	67 ± 6	1	5
	Mn	409 ± 2	420 ± 40	2	5
	Co	11.1 ± 0.4	11 ± 1	0.2	5
	Zn	109 ± 14	105 ± 9	20 to 40	20
	Ga	16.7 ± 0.9	12 ± 2	1	10
	As	11.7 ± 0.4	13 ± 2	0.5	7
	Rb	116 ± 7	116 ± 8	20	10
	Sb	2.45 ± 0.14	2.53 ± 0.09	0.1	10
	Cs	7.1 ± 0.3	7.9 ± 0.7	0.5	10
	La	32.6 ± 0.9	30 ± 2	1	5
	Ce	55 ± 2	64 ± 6	1	7
	Sm	5.1 ± 0.3	5.3 ± 0.4	0.2	7
	Eu	1.26 ± 0.04	1.2 ± 0.1	0.08	10
	Tb	0.65 ± 0.06	0.72 ± 0.06	0.06	15
	Dy	4.2 ± 0.4	4.3 ± 0.8	0.3	12
	Yb	2.07 ± 0.14	2.5 ± 0.3	0.3	10
	Lu	0.40 ± 0.04	0.40 ± 0.07	0.08	15
	Hf	5.0 ± 0.3	4.4 ± 0.2	0.5	10
	Ta	0.85 ± 0.03	0.93 ± 0.09	0.2	10
	Th	9.55 ± 0.48	10 ± 1	0.2	5
XRF	TiO ₂ (%)	0.60 ± 0.05	0.63 ± 0.06	100	8
XES	Zr	163 ± 5	160 ± 25	5	6

*Mean result and standard deviation from seven determinations by INAA, three determinations by XRF or XES

†From values compiled in Gladney and Goode (1981) and in Abbey (1982)

stitute for potassium, and the amount of potassium in the K-bentonites varies with their diagenetic history. Furthermore, manganese levels in the K-bentonites are influenced by the presence of calcite. For these reasons, the lowest nine were dismissed from the list of reliable discriminating elements.

Data on the remaining 17 elements were subjected to stepwise discriminant analysis. The first ranked element, ytterbium, was entered into the analysis. The program continued with sequential selection of the next element that, in combination with the element or elements already selected, effected the best separation among the group centroids (highest overall multivariate F ratio or minimum Wilks' lambda). The procedure continued until adding more elements did not effect further significant separation between the beds, or, in other words, add significantly to the discriminating power of the set.

The discriminant model used 15 of the 17 elements. Dysprosium and ytterbium have very similar chemical behavior. When combined in the statistical test with the other key elements, dysprosium contributed more discriminating power to the set; therefore, ytterbium was displaced. At the end of the stepwise analysis arsenic did not contribute to further separation of the groups; therefore, it also was not used. The power of discriminant analysis lies in the fact that the combination of elements, each of which has some low to moderate discriminating power, achieves discrimination superior to that of any single element.

CHEMISTRY OF THE K-BENTONITES

Concentrations of the 26 elements determined in the K-bentonite samples are listed in table 2. Results of standard rock analysis of some samples for a few major and minor

Table 2. Chemical results on K-bentonites

Sample No.	Loc.	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)	Cr (ppm)	Mn (ppm)	Co (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Rb (ppm)	Zr (ppm)	Sh (ppm)	Cs (ppm)	La (ppm)	Ce (ppm)	Sm (ppm)	Eu (ppm)	Th (ppm)	Dy (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)	Th (ppm)
Detrital																											
*RK-192	1	0.066	6.50	0.53	1.13	8.1	4.7	3.4	0.8	150	29	1.8	72	304	<0.1	3.2	5.8	12	1.1	0.17	0.23	1.6	1.2	0.19	11	1.9	27
*RK-193	2	0.066	6.50	0.53	1.13	8.1	4.7	3.4	0.8	150	29	1.8	72	304	<0.1	3.2	5.8	12	1.1	0.17	0.23	1.6	1.2	0.19	11	1.9	27
*RK-291	3	0.021	11.96	0.52	0.91	6.0	6.3	5.3	1.1	95	20	3.2	65	249	<0.1	1.9	6.2	14	1.3	0.32	0.35	2.3	1.2	0.22	0.5	1.5	24
*RK-293	4	0.022	11.73	0.38	0.83	5.2	3.4	3.6	1.0	31	3.1	3.1	70	170	<0.1	2.9	6.2	11	1.3	0.19	0.22	1.6	0.97	0.14	6.4	1.6	17
*RK-19	5	0.041	11.13	0.41	1.07	5.6	2.9	12.0	2.4	22	2.8	67	196	<0.1	2.6	7.7	13	1.7	1.5	0.21	0.22	1.8	0.96	0.2	6.6	1.6	21
*RK-19	6	0.041	11.62	0.41	1.30	5.9	3.2	19	1.5	32	1.2	1.2	67	196	<0.1	3.4	4.3	7.7	1.5	0.18	0.20	1.4	0.91	0.17	7.3	1.4	14
*RK-87	7	0.024	9.55	0.47	1.10	6.3	5.7	2.4	1.9	76	22	3.3	71	209	<0.2	2.7	11	20	1.9	0.25	0.27	2.2	1.1	0.23	7.1	1.9	26
*RK-8	8	0.022	10.47	0.57	1.14	6.0	8.6	19	0.7	190	23	5.4	69	234	0.3	3.6	3.9	7.3	1.3	0.17	0.2	1.8	1.1	0.1	8.9	1.7	19
*RK-228	10	0.022	8.99	0.72	1.20	9.3	12	8.7	1.4	25	6.2	6.2	87	387	0.3	5.0	7.6	14	2.0	0.21	0.3	1.8	1.4	0.2	15	1.9	15
*RK-229	11	0.022	11.95	0.58	0.99	6.2	8.9	13.0	0.82	33	11.2	75	365	<0.1	3.5	3.4	7.6	21	0.94	0.10	0.13	1.1	0.87	0.16	10	1.7	15
*RK-229	12	0.022	11.95	0.58	0.99	6.2	8.9	13.0	0.82	33	11.2	75	365	<0.1	3.5	3.4	7.6	21	0.94	0.10	0.13	1.1	0.87	0.16	10	1.7	15
*RK-229	13	0.021	6.32	0.88	1.13	8.4	14	120	4.1	66	29	13	79	186	0.6	3.4	6.8	7.9	0.94	0.12	0.2	2.0	0.4	0.17	1.6	1.8	16
*RK-229	14	0.021	12.23	0.40	1.35	4.7	3.4	5	0.96	29	17	4.9	75	186	<0.3	3.4	4.8	7.9	0.94	0.12	0.2	2.0	0.4	0.17	1.6	1.8	16
*W1-1	15	0.079	8.49	0.37	1.31	5.4	42	190	1.2	31	11	1.5	70	74	<0.3	2.0	14	20	1.9	0.4	0.2	1.5	0.7	0.1	2.6	0.5	9.0
*W1-2	16	0.039	14.12	0.41	2.70	4.1	21	75	4.3	140	12	5.0	82	176	0.4	2.2	10	17	1.8	0.3	0.3	2.1	1.3	0.2	6.8	1.6	20
*W1-3	17	0.039	13.70	0.41	2.70	4.1	21	75	4.3	140	12	5.0	82	176	0.4	2.2	10	17	1.8	0.3	0.3	2.1	1.3	0.2	6.8	1.6	20
*W1-4	18	0.023	8.50	0.64	1.23	8.4	9.0	17	0.9	50	13	6.7	88	387	<0.4	7.2	6.0	13	1.7	0.23	0.27	1.9	1.4	0.2	7.2	1.3	15
*W9-1	19	0.027	13.83	0.39	1.86	4.2	6.5	28	3.5	57	13	8.7	74	209	<0.3	3.3	5.1	10	1.5	0.2	0.2	1.7	1.0	0.2	7.2	1.3	15
*W7-1	20	0.039	14.12	0.41	2.70	4.1	21	75	4.3	140	12	5.0	82	176	0.4	2.2	10	17	1.8	0.3	0.3	2.1	1.3	0.2	6.8	1.6	20
*W7-2	21	0.039	14.12	0.41	2.70	4.1	21	75	4.3	140	12	5.0	82	176	0.4	2.2	10	17	1.8	0.3	0.3	2.1	1.3	0.2	6.8	1.6	20
*W7-3	22	0.029	15.50	0.28	2.32	3.2	4.8	27	2.9	35	11	6.5	59	162	<0.3	1.3	6.8	11	1.5	0.3	0.3	2.2	1.3	0.2	5.5	1.3	19
*W6-1	23	0.027	13.99	0.52	1.48	5.8	10	96	2.9	35	11	4.7	71	238	<0.4	2.2	8.5	20	1.9	0.3	0.3	2.2	1.3	0.2	5.5	1.3	19
*W6-2	24	0.027	14.61	0.27	1.69	5.0	5.6	61	0.4	190	9.4	6.8	57	184	0.3	1.0	20	43	3.4	0.6	0.5	3.6	1.8	0.2	5.9	1.3	21
*W6-3	25	0.027	14.61	0.27	1.69	5.0	5.6	61	0.4	190	9.4	6.8	57	184	0.3	1.0	20	43	3.4	0.6	0.5	3.6	1.8	0.2	5.9	1.3	21
*W6-4	26	0.027	14.61	0.27	1.69	5.0	5.6	61	0.4	190	9.4	6.8	57	184	0.3	1.0	20	43	3.4	0.6	0.5	3.6	1.8	0.2	5.9	1.3	21
*W6-5	27	0.027	14.61	0.27	1.69	5.0	5.6	61	0.4	190	9.4	6.8	57	184	0.3	1.0	20	43	3.4	0.6	0.5	3.6	1.8	0.2	5.9	1.3	21
*W6-6	28	0.027	14.61	0.27	1.69	5.0	5.6	61	0.4	190	9.4	6.8	57	184	0.3	1.0	20	43	3.4	0.6	0.5	3.6	1.8	0.2	5.9	1.3	21
*W6-7	29	0.027	14.61	0.27	1.69	5.0	5.6	61	0.4	190	9.4	6.8	57	184	0.3	1.0	20	43	3.4	0.6	0.5	3.6	1.8	0.2	5.9	1.3	21
*W6-8	30	0.026	8.49	0.38	2.46	7.8	5.4	55	8.3	76	23	7.8	100	196	<0.3	5.0	16	31	2.4	0.40	0.48	2.9	1.6	0.2	8.5	1.8	16
*W6-9	31	0.026	8.49	0.38	2.46	7.8	5.4	55	8.3	76	23	7.8	100	196	<0.3	5.0	16	31	2.4	0.40	0.48	2.9	1.6	0.2	8.5	1.8	16
*W6-10	32	0.029	15.50	0.28	2.32	3.2	4.8	27	2.9	35	11	6.5	59	162	<0.3	1.3	6.8	11	1.5	0.3	0.3	2.2	1.3	0.2	5.5	1.3	19
*W6-11	33	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-12	34	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-13	35	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-14	36	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-15	37	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-16	38	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-17	39	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-18	40	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-19	41	0.025	7.97	0.44	3.06	8.0	5.2	12	1.2	220	25	8.6	100	277	<0.5	9.1	6.3	13	1.9	0.3	0.4	3.1	1.6	0.3	9.6	1.7	26
*W6-20	42	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-21	43	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-22	44	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-23	45	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-24	46	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-25	47	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-26	48	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-27	49	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-28	50	0.027	8.56	0.41	2.82	5.9	6.0	150	9.8	45	21	10	82	188	<0.5	4.2	7.9	16	1.6	0.22	0.23	1.9	0.99	0.19	9.7	2.0	23
*W6-29	51	0.033	9.13	0.74	0.38	11	8.3	4	0.4	20	0.5	110	319	<0.2	14	19	38	4.3	0.5	0.7	3.6	2.1	0.3	11	2.0	30	
*W6-30	52	0.031	10.05	0.52	0.53	6.1	15	27	8.9	110	17	1.3															

Table 2. Continued

Sample No.	Loc.	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	Sc (ppm)	Cr (ppm)	Mn (ppm)	Co (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Rb (ppm)	Zr (ppm)	Sb (ppm)	Cs (ppm)	La (ppm)	Ce (ppm)	Sn (ppm)	Eu (ppm)	Tb (ppm)	Oy (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)	Th (ppm)	
Milbrig																												
*001	29	0.041	10.17	0.12	1.98	8.1	5.1	58	4.2	36	14	4.9	66	173	0.2	2.9	3.7	8.6	1.4	0.21	0.22	1.8	1.1	0.20	8.9	2.1	18	15
*002	30	0.039	9.28	0.20	1.98	6.8	5.7	23	1.9	69	25	2.7	93	221	0.2	5.1	3.9	6.7	0.98	0.16	0.21	1.2	0.22	0.99	0.18	7.4	1.8	19
*003	31	0.031	10.93	0.24	1.10	9.3	9.3	38	3.0	37	26	3.1	91	205	0.1	5.9	7.0	15	1.7	0.28	0.24	1.0	0.3	0.8	1.8	1.8	21	18
*004	32	0.039	7.12	0.21	1.09	7.9	3.0	28	1.4	24	25	4.5	90	200	<0.4	5.1	3.9	8.7	1.2	0.16	0.23	1.7	1.1	0.24	9.2	2.1	18	18
*005	33	0.045	13.25	0.20	1.50	5.8	5.7	21	0.6	39	14	7.1	61	107	0.2	6.3	5.6	32	0.1	0.2	0.3	1.2	0.2	0.4	4.5	1.7	19	19
*006	34	0.045	13.25	0.20	1.50	5.8	5.7	21	0.6	39	14	7.1	61	107	0.2	6.3	5.6	32	0.1	0.2	0.3	1.2	0.2	0.4	4.5	1.7	19	19
*007	35	0.037	7.55	0.21	1.80	6.5	3.7	20	0.9	630	26	11	96	159	1.4	5.2	1.8	3.5	0.6	0.11	0.1	0.2	0.9	0.2	7.0	2.1	19	19
*008	36	0.041	8.38	0.21	1.35	7.8	6.4	91	7.0	...	24	6.4	84	127	<0.5	3.9	7.8	17	2.1	0.31	0.3	2.4	1.8	0.3	6.0	2.0	30	30
*009	37	0.040	7.56	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*010	38	0.043	8.00	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*011	39	0.043	8.00	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*012	40	0.043	8.00	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*013	41	0.043	8.00	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*014	42	0.043	8.00	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*015	43	0.043	8.00	0.20	1.22	8.0	4.8	88	4.5	...	25	5.6	81	136	0.3	4.7	5.2	15	1.8	0.25	0.26	2.0	1.6	0.29	6.4	2.0	30	30
*016	44	0.048	9.06	0.26	1.74	6.8	13	90	7.1	38	17	5.1	76	189	<0.5	4.2	7.6	14	1.5	0.28	0.26	1.9	1.2	0.23	8.2	1.8	14	14
*017	45	0.044	10.03	0.27	1.65	7.6	14	90	12	...	21	22	81	177	0.5	4.7	7.9	12	1.2	0.24	0.2	1.6	0.97	0.2	4.9	1.7	17	17
*018	46	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*019	47	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*020	48	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*021	49	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*022	50	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*023	51	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*024	52	0.044	6.98	0.22	1.32	7.7	3.9	97	...	160	25	9.8	76	167	0.4	5.7	3.0	5.5	0.8	0.14	0.2	1.5	1.4	0.15	7.4	2.0	17	17
*025	53	0.053	10.26	0.24	1.11	7.2	4.8	9	0.5	...	15	7.1	100	156	0.5	11	1.2	2.0	0.3	0.07	0.07	0.5	0.7	0.1	7.1	2.1	16	16
*026	54	0.034	8.86	0.22	2.27	6.5	9.3	47	1.0	...	17	7.3	95	160	0.5	11	1.2	2.0	0.3	0.07	0.06	0.62	0.65	0.13	9.5	1.9	16	16
*027	55	0.033	9.79	0.26	2.21	6.8	4.0	11	0.79	63	16	19	110	204	0.5	18	2.9	5.1	1.1	0.14	0.2	1.4	1.2	0.2	9.1	2.0	19	19
*028	56	0.039	11.28	0.25	2.66	6.0	2.6	41	2.8	...	14	12	88	191	0.6	9.8	1.4	2.3	0.33	0.07	0.03	0.40	0.61	0.1	9.1	2.0	19	19
*029	57	0.038	8.89	0.33	0.89	7.1	3.7	7.5	0.7	...	16	10	130	229	0.7	26	2.0	3.5	0.5	0.07	0.06	0.7	0.9	0.2	11	2.2	17	17
*030	58	0.034	8.86	0.22	2.27	6.5	9.3	47	1.0	...	17	7.3	95	160	0.5	11	1.2	2.0	0.3	0.07	0.06	0.62	0.65	0.13	9.5	1.9	16	16
*031	59	0.034	8.86	0.22	2.27	6.5	9.3	47	1.0	...	17	7.3	95	160	0.5	11	1.2	2.0	0.3	0.07	0.06	0.62	0.65	0.13	9.5	1.9	16	16
*032	60	0.034	8.86	0.22	2.27	6.5	9.3	47	1.0	...	17	7.3	95	160	0.5	11	1.2	2.0	0.3	0.07	0.06	0.62	0.65	0.13	9.5	1.9	16	16
*033	61	0.034	8.86	0.22	2.27	6.5	9.3	47	1.0	...	17	7.3	95	160	0.5	11	1.2	2.0	0.3	0.07	0.06	0.62	0.65	0.13	9.5	1.9	16	16
*034	62	0.031	7.65	0.23	2.32	8.6	2.6	7.3	0.0	...	19	7.9	140	249	0.3	36	7.9	19	2.8	0.27	0.3	2.1	1.5	0.3	9.5	1.9	23	23
*035	63	0.031	7.65	0.23	2.32	8.6	2.6	7.3	0.0	...	19	7.9	140	249	0.3	36	7.9	19	2.8	0.27	0.3	2.1	1.5	0.3	9.5	1.9	23	23
*036	64	0.031	7.65	0.23	2.32	8.6	2.6	7.3	0.0	...	19	7.9	140	249	0.3	36	7.9	19	2.8	0.27	0.3	2.1	1.5	0.3	9.5	1.9	23	23
*037	65	0.031	7.65	0.23	2.32	8.6	2.6	7.3	0.0	...	19	7.9	140	249	0.3	36	7.9	19	2.8	0.27	0.3	2.1	1.5	0.3	9.5	1.9	23	23
*038	66	0.039	7.29	0.25	0.47	9.0	2.3	1.8	1.8	...	20	0.8	170	176	<0.2	40	3.8	7.3	1.1	0.15	0.1	1.2	1.0	0.2	7.7	1.9	22	22
*039	67	0.026	5.21	0.27	0.61	8.4	4.3	5.8	0.3	...	18	0.76	120	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*040	68	0.026	5.21	0.27	0.61	8.4	4.3	5.8	0.3	...	18	0.76	120	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*041	69	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*042	70	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*043	71	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*044	72	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*045	73	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*046	74	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*047	75	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*048	76	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*049	77	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52	0.7	1.1	0.22	8.3	1.9	22	22
*050	78	0.023	4.36	0.28	2.44	8.3	4.1	3.0	1.2	...	19	8.0	96	211	<0.2	24	8.8	20	1.7	0.26	0.52</							

elements are presented in table 3. Table 4 lists the mean concentration and standard deviation for each of the 26 elements in table 2 by bed in the control group of 60 samples. The following is a discussion of the geochemical characteristics that permit chemical fingerprinting of the four Decorah K-bentonite beds, based on the control group samples.

A study of table 4 reveals the elements likely to serve as discriminators of differences in chemical composition between K-bentonite beds. These are the elements with different mean concentrations from bed to bed and a relatively small range of concentration within a bed. On the basis of the results of analysis of variance, we can arrange the elements with similar chemistry in groups and rank them from good discriminating power to none, as follows: a) Zr, Ti, Hf, and Ta; b) the rare earth elements, heavy to light—Yb, Dy, Lu, Tb, Eu, Sm, La, Ce; c) Sc; d) Na; e) Th; f) Fe, As, and Sb; g) K, Rb, Cs, Ga; h) Co, Cr, Mn, and Zn. The elements will be discussed approximately in order of these groupings.

Data on some of the most discriminating elements were

Table 3. Data on major and minor elements in selected K-bentonites

Sample number	Locality	SiO ₂ (%)	Al ₂ O ₃ (%)	CaO (%)	P ₂ O ₅ (%)
Deicke					
*DRK-228	10	59.3	24.3	0.9	0.18
MV11-1	15	33.9	10.8	22.8	0.1
*DRK-202	17			0.5	0.12
*MV9-1	19			0.5	0.17
*MV6-1	23			0.4	0.16
DRK-193	40			9.8	0.08
DRK-191	42	58.6	22.7	0.7	0.1
DRK-236	57			1.3	0.17
DRK-239	62				(0.19)†
DRK-213	66			0.8	0.14
DRK-211	67	56.3	22.0	0.7	0.1
Millbrig					
*MKB-30	1	58.0	20.2	3.3	0.1
*MV3-1	34			0.3	0.07
DRK-248	39	58.4	21.7	1.9	0.1
DRK-274	50			0.4	0.14
DRK-234	62	57.5	22.2	0.9	0.1
DRK-268	64	53.9	21.2	7.9	<0.1
DRK-241	65	52.7	21.2	6.4	<0.1
Unassigned Decorah K-bentonites					
DRK-247	15	56.4	25.1	1.1	0.1
DRK-223	52			0.5	0.07
DRK-224	52	55.1	22.6	0.7	0.15
DRK-222	53	43.2	12.9	16.6	0.46
DRK-243	54			0.5	0.15
DRK-235	57			0.8	0.15
DRK-238	58	53.4	20.4	3.3	0.1
DRK-208	60			0.7	0.31
DRK-245	62			1.2	0.24
DRK-271	63			3.5	0.17
DRK-210	65	50.1	16.6	7.0	0.1
Other K-bentonites					
DRK-265	64	52.6	20.2	3.8	0.43

*Control group sample

†Powder sample

plotted in bivariate diagrams (figs. 7 to 9) to show the clustering of samples by bed. Not every discriminating element has a distinguishing concentration in each bed. But as can be seen from figure 7, sodium helps to distinguish the Deicke from the Millbrig and Dickeyville K-bentonites, and these from the Elkport. The concentrations of dysprosium (fig. 7), ytterbium (fig. 8), and the other heavy rare earth elements are significantly higher in the Elkport and Dickeyville K-bentonites than in the Deicke, and tend to be somewhat higher in the Deicke than in the Millbrig. Hafnium and zirconium concentrations increase from Millbrig to Deicke to Elkport and Dickeyville, and tantalum is generally higher in the Millbrig than in the other three

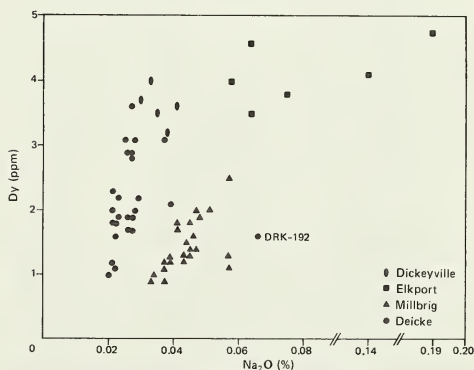


Figure 7. Distribution by bed of sodium and dysprosium in the control group samples of the Decorah K-bentonites.

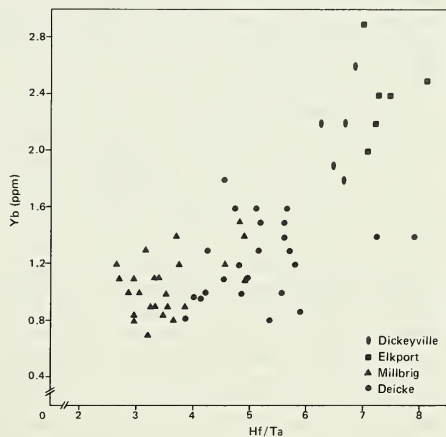


Figure 8. Distribution by bed of the ratio of hafnium to tantalum contents and of ytterbium in the control group samples of the Decorah K-bentonites.

Table 4. Mean and standard deviation of elemental concentrations in control group samples (values in ppm unless otherwise noted)

Element	Deicke (25)*	Millbrig (24)	Elkport (6)	Dickeyville (5)
Na ₂ O (%)	0.027 ± 0.009	0.044 ± 0.007	0.100 ± 0.055	0.035 ± 0.005
K ₂ O (%)	11.0 ± 2.9	9.4 ± 2.0	9.2 ± 0.7	7.3 ± 0.4
TiO ₂ (%)	0.46 ± 0.14	0.22 ± 0.06	0.52 ± 0.06	0.43 ± 0.15
Fe ₂ O ₃ (%)	2.2 ± 1.4	1.4 ± 0.4	3.9 ± 0.6	2.1 ± 1.1
Sc	6.2 ± 1.9	7.9 ± 1.1	14.0 ± 1.7	12.1 ± 2.0
Cr	7.1 ± 3.9	7.2 ± 5.9	12.3 ± 5.1	11.3 ± 18.9
Mn	57 ± 57	54 ± 36	141 ± 82	59 ± 50
Co	3.1 ± 2.5	4.0 ± 2.5	12.2 ± 5.7	4.2 ± 5.7
Zn	144 ± 157(18)	110 ± 176(11)	137 ± 101(5)	81 (1)
Ga	20 ± 6	21 ± 4	21 ± 2	26 ± 3
As	6.8 ± 3.4	4.5 ± 2.4	11.3 ± 4.4	8.6 ± 4.8
Rb	76 ± 12	85 ± 12	90 ± 5	85 ± 10
Zr	237 ± 68	161 ± 33	355 ± 25	354 ± 45
Sb	<0.3 ± 0.1	<0.3 ± 0.3	0.6 ± 0.1	0.6 ± 0.3
Cs	3.6 ± 2.0	4.6 ± 1.6	4.7 ± 0.3	5.9 ± 2.1
La	9.0 ± 4.8	5.1 ± 3.8	6.7 ± 1.9	5.1 ± 4.6
Ce	16.8 ± 9.6	10.0 ± 7.0	12.8 ± 3.7	10.0 ± 8.0
Sm	1.8 ± 0.7	1.3 ± 0.4	2.0 ± 0.5	1.9 ± 0.4
Eu	0.26 ± 0.12	0.20 ± 0.10	0.49 ± 0.08	0.41 ± 0.07
Tb	0.28 ± 0.09	0.21 ± 0.08	0.45 ± 0.10	0.43 ± 0.08
Dy	2.1 ± 0.7	1.4 ± 0.4	4.1 ± 0.5	3.6 ± 0.3
Yb	1.2 ± 0.3	1.1 ± 0.2	2.4 ± 0.3	2.1 ± 0.3
Hf	0.22 ± 0.04	0.20 ± 0.07	0.47 ± 0.06	0.42 ± 0.07
Ta	8.8 ± 2.5	7.1 ± 1.2	12.7 ± 1.0	11.6 ± 1.1
Th	1.7 ± 0.3	2.0 ± 0.2	1.7 ± 0.2	1.8 ± 0.1
Th	20 ± 5	16 ± 4	21 ± 1	21 ± 2

*Number of samples in parentheses

K-bentonites (table 4). The ratio of hafnium to tantalum then provides some separation of each of the four beds (fig. 8).

Scandium is higher in the Elkport and Dickeyville than in the Deicke and Millbrig K-bentonites and helps to place a sample in one of two beds versus the other two (fig. 9). Titanium is significantly lower in the Millbrig than in the other three K-bentonites (fig. 9). Therefore, although no one element serves to delineate a K-bentonite bed completely from the others, a combination of elements can do so.

For these elements to serve as discriminators between K-bentonite beds, their concentrations must have been different in the separate volcanic ash falls, and they must have been preserved or altered consistently in the transformation from volcanic ash to K-bentonite. The concentrations of certain elements could have been different in the separate volcanic ash falls if the falls represented eruptions from different volcanoes or sets of volcanoes, or eruptions from volcanoes having a magma source that gradually changed over time.

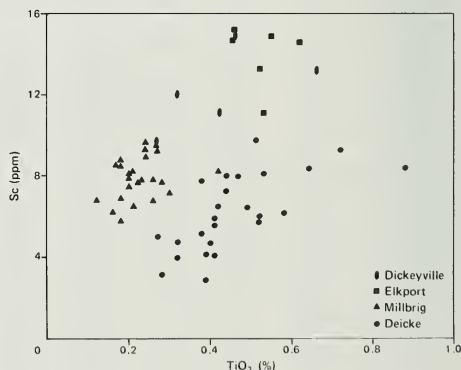


Figure 9. Distribution by bed of titanium and scandium in the control group samples of the Decorah K-bentonites.

Just as immobile elements serve to differentiate volcanic rocks from different magma series (Pearce and Cann, 1973; Pearce, 1975; Winchester and Floyd, 1977; Wood, Joron, and Treuil, 1979), these same elements should be most useful in distinguishing volcanic ashes arising from different magmas. Immobile elements are expected in the accessory as well as the primary minerals of volcanic ash and altered volcanic ash. Minerals that probably have remained unaltered from the original ash in the Decorah K-bentonites of the Upper Mississippi Valley include euhedral zircon, euhedral apatite, hornblende, biotite, and sanidine (Allen, 1929, 1932; Mossler and Hayes, 1966). Some portion of the discriminating elements zirconium and hafnium will be found in the zircon. The principal residence of titanium and some of the tantalum is probably a heavy mineral like magnetite or ilmenite. Allen (1929, 1932) found magnetite in the Decorah K-bentonites. Westgate and Fulton (1975) found ilmenite and titanian magnetite in Quaternary tephra in British Columbia; Weaver (1953) found leucoxene, an alteration product of ilmenite, in Ordovician K-bentonites from Pennsylvania.

Some of the rare earth element and thorium content of the K-bentonites is contained in accessory minerals such as apatite and zircon. However, most of the rare earth element content of rocks is associated with the major and minor rock-forming minerals, rather than with accessory minerals in which rare earth elements are concentrated (Haskin and Schmitt, 1967). Therefore, most of the rare earth element content should be associated with unaltered minor minerals such as hornblende, or with the bulk aluminosilicate material of the volcanic ash that was altered to mixed-layer clays and/or feldspar.

The rare earth elements do not have a consistent (chondrite-normalized) relative distribution pattern in the four beds. The relative distribution pattern for the Deicke control group ($\text{La/Yb} = 7.5$) is similar to that for the North American shale composite ($\text{La/Yb} = 10.3$) of Haskin et al. (1968). The Elkport and Dickeyville Beds have the highest concentrations of heavy rare earth elements (table 2), but the ratio of light to heavy rare earth elements for the control group samples decreases in the following order: Deicke, Millbrig ($\text{La/Yb} = 5.1$), Elkport ($\text{La/Yb} = 2.8$), and Dickeyville ($\text{La/Yb} = 2.4$). The heavier rare earth elements would be affected less than the lighter ones during alteration of the host minerals (Haskin and Schmitt, 1967). The lighter rare earth elements lanthanum and cerium have much wider within-bed range (table 4) than do the heavy rare earth elements. In addition, some K-bentonite samples collected from Missouri were much more enriched in the lighter rare earth elements than the control group samples from the northern outcrop area. The rare earth element chemistry probably represents original ash composition with some modification during diagenesis.

The scandium in these K-bentonites could have been

associated with ferromagnesian silicates (Goldschmidt, 1954) such as biotite in the volcanic ash.

Because sodium is a very mobile element, finding that it was such a valuable discriminant element (as shown in the bivariate plot in fig. 7) was unexpected. The uniform sodium levels observed in the Elkport and Dickeyville Beds could reflect the small number of samples analyzed from each bed; however, the Deicke and Millbrig K-bentonites, for which we had numerous samples, were also uniform in sodium. Concentrations in outcrop samples were within 30% of the mean values of 0.027% Na_2O in the Deicke and 0.044% Na_2O in the Millbrig. Samples that had anomalous sodium contents proved upon further testing to be of poor quality. For example, Deicke sample MV11-1 ($\text{Na}_2\text{O} = 0.079\%$) contained calcite ($\text{CaO} = 22.8\%$). Deicke control group sample DRK-192 ($\text{Na}_2\text{O} = 0.066\%$), which is displaced to the right of the main cluster of samples on the sodium versus dysprosium diagram (fig. 7), was from an old and weathered outcrop. It likely has been affected by surface organic and inorganic processes. A few anomalous values did skew the sodium distribution, however, so that sodium was not a strong component in the statistical analysis.

The fact that sodium occurs in such low concentration and yet differs significantly between beds suggests that all soluble sodium was removed during the formation of these K-bentonites and that the small amount remaining is present in a resistant crystalline phase contained in the original ash, rather than present as an adsorbed hydrated ion on clay minerals. Allen (1929, 1932) and Mossler and Hayes (1966) found sanidine in the Mississippi Valley K-bentonites. The corresponding sodium-bearing mineral high-temperature albite could also be expected (the amount would be too small for detection in X-ray diffraction analysis) or there could be sodium substitution in the sanidine. Byström (1956) found trace amounts of primary plagioclase and sodium substitution in sanidine in the Ordovician K-bentonites at Kinnekulle, Sweden.

Sodium is not valid as a discriminating element with respect to core samples (DRK-211, -272 to -276); core samples contain more sodium than outcrop samples, probably as dissolved solids in porewater.

Some elements determined routinely by instrumental neutron activation analysis are those involved in the alteration of volcanic ash to K-bentonite or K-feldspar. Foremost among these is potassium. It is generally agreed (Hoffman and Hower, 1979) that bentonite is formed by devitrification of volcanic ash, and that a variable amount of potassium is added to the smectite clay (bentonite) during formation of the mixed-layer illite/smectite clay (K-bentonite). Weiss (1954) thought there was further alteration of K-bentonite to K-feldspar in the upper part of the Galena Group, but Hay (1966) considered that some tephra probably alter first to a potassium-zeolite (clinoptilolite) and then to feldspar.

Potassium concentrations in the Decorah K-bentonites range from 6% to 15.5% K_2O . X-ray diffraction analyses indicated that those samples with a high K_2O content had a correspondingly high K-feldspar content. The effect of a wide range of potassium in the samples studied here is illustrated in the bivariate plot of scandium and potassium in all the Decorah K-bentonite samples (fig. 10). With significant K-feldspar content in a sample (K_2O content above approximately 8%), scandium content is significantly decreased. (Note, however, that scandium levels were consistently higher in Elkport and Dickeyville samples than in Deicke and Millbrig samples of similar potassium content. This enabled scandium to be a discriminant element for these beds even though its concentration depends upon the ratio of mixed-layer clay to K-feldspar.) High K-feldspar levels in the samples were associated with low levels of several other elements. Correlation analyses by bed of the chemical elements in the set of 60 control group samples showed that potassium correlates negatively with Ga (within-group pooled correlation coefficient $r = -0.87$), Ta (-0.70), Sc (-0.69), Cs (-0.64), Hf (-0.60), Zr (-0.55), Ti (-0.54), Rb (-0.48), and Th (-0.40). All correlations were significant at the 95% confidence level.

Among the control group samples, the Deicke is the K-bentonite with the greatest range of potassium content,

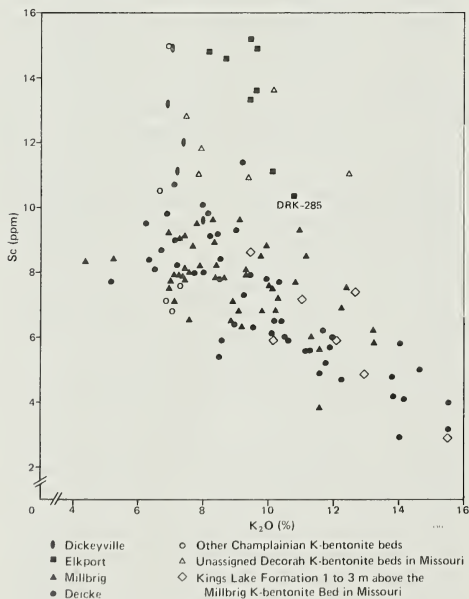


Figure 10. Variation of scandium with potassium content in all samples of K-bentonites from the Upper Mississippi Valley. The sample DRK-285 of Elkport K-bentonite with highest potassium content is discussed in the text.

from $K_2O = 6.32\%$ to 15.52% . The relationship between decreased concentrations of some discriminating elements and increased K-feldspar content tends to spread out the Deicke samples in scatter plots of these elements, as seen, for example, in the plot of scandium and titanium data (fig. 9). This effect also causes some of the spread in the Millbrig cluster in such plots because some of the control group samples of that bed also contain appreciable K-feldspar (values of K_2O as high as 13.22%).

Gallium substitutes in trace amounts for aluminum in minerals. K-bentonite of average mixed-layer clay composition contains about $20\% Al_2O_3$ (Huff and Türkmenoglu, 1981), and orthoclase K-feldspar has $18.4\% Al_2O_3$. Therefore, a small negative correlation of gallium with K-feldspar content in these samples is reasonable. On the other hand, rubidium and cesium substitute in trace amounts for potassium in all its minerals, so a positive correlation between concentrations of potassium and rubidium and cesium would be expected. However, the negative correlation that we obtained means that cesium and rubidium were not taken up in the K-feldspar in these samples. This may indicate formation of the K-feldspar by low-temperature recrystallization, with loss of alumina, from illite (Horstman, 1957) or even from mixed-layer clay precursors. The negative correlations between potassium and the other elements listed may be partly attributable to the diluent effect on other minerals of the higher K-feldspar content in the samples; however, such strong negative correlations may also indicate that these other trace elements, including gallium, are also shed from substitution or adsorption sites in precursor minerals during their transformation to K-feldspar.

Iron occurs in authigenic pyrite (Mossler and Hayes, 1966) or in limonite (Willman and Kolata, 1978) in these K-bentonites. Arsenic and antimony are associated with iron, having correlation coefficients $r(Fe, As)$, $r(Fe, Sb)$, and $r(As, Sb)$ of 0.6 to 0.7 for the control group of 60 K-bentonite samples. This is consistent with the dominant occurrence of the chalcophilic arsenic and antimony as trace substituents in pyrite. Iron, arsenic, and antimony contents are lowest in the Millbrig and highest in the Elkport K-bentonite (table 2). However, the question arises as to whether these three elements can be relied upon as discriminators for the beds over wide geographic areas. We have no evidence that their differences between beds reflect a consistent pattern of alteration from volcanic ash to K-bentonite, as opposed to alteration dependent upon local or regional diagenetic or later weathering conditions.

Borchardt et al. (1971) and Randle et al. (1971) found cobalt to be useful for discriminating between ash deposits from volcanoes in the Cascade Mountains. Pearce (1975) used chromium as one of a set of elements to discriminate between lava rocks with different magma sources. In the control group of K-bentonites in this study, cobalt and chromium have different mean values in different beds. For example, mean cobalt content is significantly higher in

the Elkport than in the other three K-bentonites (table 4). But cobalt and chromium also have a wide range of values in each bed, so that chromium has no power, and cobalt only weak discriminating power. In the chemical correlation of these four Decorah K-bentonites made in the preliminary study by Kolata et al. (1983) on the basis of a control group of only 25 samples, cobalt and chromium appeared among the top six discriminating elements of the statistical model. It is evident now that cobalt and chromium were poorly defined in that study, particularly in the Elkport and Dickeyville K-bentonite Beds.

Manganese and zinc also have wide ranges of concentration in each of the four K-bentonites. Manganese content was low (<30 ppm) in most samples, but this element is greatly concentrated in limestone (Goldschmidt, 1954), so that even slight contamination of a sample by limestone gives a manganese concentration of 100 ppm or more. Zinc is a mobile element in diagenetic processes. For these reasons, manganese and zinc are not useful as discriminant elements, although their concentration levels can give useful information about the diagenetic environment of the K-bentonite sample.

Sampling

The quality of the sample is an important factor in the attempt to differentiate K-bentonite beds on the basis of their chemical composition. Where beds are thin, it is difficult to collect a sample free of the confining shale or limestone. At some localities the K-bentonites have been mixed with shale, limestone, or fossil debris. Four pairs of samples—DRK-191 and DRK-277, MKB-9 and DRK-291, MKB-3 and DRK-187, and MKB-11 and DRK-226—illustrate reproducible sampling. Samples in each set were collected from two different places in a bed at one locality on different dates. They did not differ significantly in chemical composition (table 2).

Weathering

The effect of weathering on chemical composition of the K-bentonites is also noticeable. For example, samples DRK-234, -259, and -233 collected from the Millbrig K-bentonite bed at locality 62 represent a gradation within a distance of 1 m from less weathered to more weathered. DRK-234 is a medium gray, hard clay; DRK-259 is a dark yellowish orange plastic clay; and DRK-233 is a very pale orange, very soft clay. As shown in table 2, the three samples have similar potassium contents and similar contents of the discriminating elements Ti, Zr, Hf, Ta, Na, and Sc. DRK-234 has the highest concentration of rare earth elements (particularly the lightest rare earth elements, lanthanum and cerium), and DRK-233 has the lowest iron, thorium, and rare earth element contents. We conclude that among the good discriminating elements we have identified, the rare earth elements (particularly the light rare earth elements) and thorium are more affected by weathering than are Ti, Zr, Hf, Ta, Sc, and Na.

STATISTICAL RESULTS

The chemical data were subjected to discriminant analysis to achieve the best chemical correlation of the K-bentonite beds. Discriminant analysis provides a method of handling data on a large number of elements, allows the data to be applied simultaneously, and is rigorous in interpretation of the data.

The discriminant analysis used three linear functions of the form

$$f = \sum_{i=1}^{15} a_i x_i$$

where a_i is a coefficient and x_i is the concentration of element i in a K-bentonite sample. The statistical properties of the three discriminant functions are shown in table 5.

Table 5. Properties of the discriminant functions for four K-bentonite beds

Function	Eigenvalue	Percent of variance	Canonical correlation
1	16.65	61.9	0.97
2	9.16	34.0	0.95
3	1.10	4.1	0.72
		100.0	

The eigenvalues, a measure of the relative amount of variance among the group of elements accounted for by each function, indicate that the third function is relatively small compared to the first two and contributes relatively little to the discriminant analysis. The first two functions include 95.9% of the variance accounted for by the model. Moreover, the canonical correlation coefficients associated with the functions show that the first two discriminant functions are each very highly correlated with the groups (or K-bentonite beds) and the third is somewhat less correlated.

The correlations show that the functions, especially the first two, are very effective at separating the four beds. Different elements are important in each of the three functions. The approximate order of importance of the elements to the discriminant model (i.e., all elements taken as a group) is: Eu, Sm, Sc, Ti, Zr, Th, Hf, Lu, Ta, Dy, Tb, Fe, Co, Na, and Sb. Terbium is redundant of heavy rare earth elements listed earlier, and the last four elements are less important. The values of each function calculated using mean elemental concentrations for each group are shown in table 6. They may be visualized as defining point coordi-

Table 6. Canonical discriminant functions evaluated at group means

Group	Function 1	Function 2	Function 3
1 (Deicke)	-3.28	2.45	0.06
2 (Millbrig)	-0.03	-3.55	0.17
3 (Elkport)	9.25	3.00	1.59
4 (Dickeyville)	5.47	1.17	-3.05

nates within a 3-dimensional orthogonal grid. The four groups have significantly different values (scores) for function 1, which may be equated to an x-axis direction. Group 2 (Millbrig) is separated from the other three in function 2 (y-axis direction), and groups 3 (Elkport) and 4 (Dickeyville) are separated in function 3 (z-axis).

The 60 control group samples were back-classified using the discriminant functions and all classified correctly into their respective groups. They would not necessarily have done so if the separation of the groups achieved by the model was so insufficient that the cluster of control group samples for one bed still overlapped that of another. In other words, we have identified by discriminant analysis a distinct chemical fingerprint for each of the K-bentonite beds, as defined by the samples in the control group, by which each control group sample can be classified correctly in its proper bed. These results are illustrated in figure 11, an x-y plot of the scores of the control group samples on the first two discriminant functions (third function set to zero). The two-dimensional plot is sufficient to illustrate the results because the third function is relatively small. Only Elkport and Dickeyville have significant value in the third dimension, and samples of Elkport and Dickeyville are a small fraction of the total number of samples.

In figure 11, the group centroids, marked by asterisks, are the mean discriminant scores for the K-bentonite beds, and the boundaries for each bed are the lines of equidistance between group centroids. Samples of each bed in the control group plot correctly into the territory defined for that bed.

The remaining group of 66 samples that were analyzed

in this investigation was collected at 36 widely distributed localities from Minnesota to Missouri. These samples were used to test the stratigraphic usefulness of fingerprinting over a more extended distance. Identification of the beds from which the samples were collected was inferred from stratigraphic position. Forty-six of the samples were collected from the Deicke and Millbrig K-bentonite Beds, particularly in western Illinois and eastern Missouri. Two samples were collected from the Elkport in the northern outcrop area. These 48 samples were classified using the functions obtained in the discriminant analysis. The value of each function for a sample was calculated by multiplying the elemental concentrations by the corresponding unstandardized discriminant coefficients. The samples were then classified into one of the four beds and plotted on the classification diagram defined by the two major discriminant functions (fig. 12). All but two samples classified correctly into their respective beds as inferred from stratigraphic position.

One must be cautious when working with unknown samples because the classification analysis will always place a sample into one of the four beds. In order for this technique to be useful it is essential to work within a firm biostratigraphic framework. An unknown K-bentonite bed must be precisely placed in its chronostratigraphic and lithostratigraphic context.

Eighteen samples, most from the Kings Lake Formation of eastern Missouri, were contaminated to some extent by shale and limestone. This contamination resulted in inconsistent elemental concentrations. Therefore, we did not classify them using the discriminant analysis.

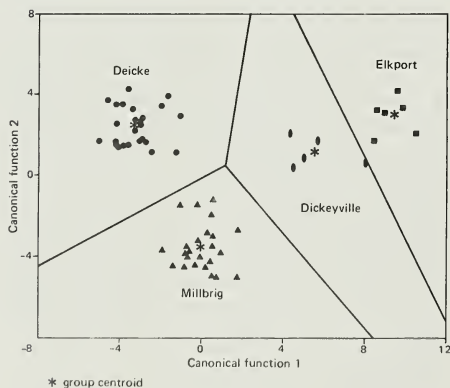


Figure 11. Territorial map constructed from the two major canonical discriminant functions calculated for 15 elements in the 60 control group samples. Asterisks mark the group centroids or means. Boundaries are defined by the loci of points equidistant from pairs of centroids.

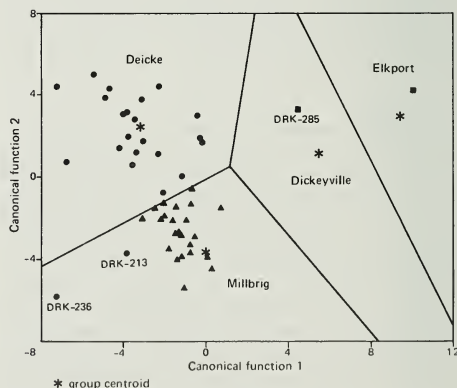


Figure 12. Classification of 48 non-control group samples of Decorah K-bentonites as illustrated by their scores for the two major canonical functions derived in the discriminant analysis. Asterisks mark the control group centroids or means.

CORRELATION OF THE K-BENTONITES

Deicke K-bentonite Bed

The Deicke K-bentonite Bed has been identified by chemical analyses in outcrop and subsurface from St. Paul, Minnesota, to at least as far south as Cape Girardeau, Missouri, a distance of about 900 km (figs. 5 and 6). Furthermore, the K-bentonite described by Witzke (1980) from the upper part of the Platteville Group near Le Mars (locality 67) in northwestern Iowa, approximately 300 km west of the Mississippi Valley region, is chemically most similar to the Deicke. Because the Deicke is the thickest and most widespread of all the Champlainian (middle Ordovician) K-bentonites in the Mississippi Valley, it seems very likely that the Le Mars occurrence is the western extension of the Deicke K-bentonite Bed.

Although the Deicke has a consistent chemical fingerprint, some variations in chemistry exist. The concentrations of thorium and the rare earth elements, which are among the elements that are useful in discriminating the Deicke, are higher in Missouri than in the northern outcrop area. Two samples, DRK-213 and DRK-236, had particularly high concentrations of the rare earth elements, ranging from nine times as much lanthanum to twice as much ytterbium as the average Deicke sample from the northern area. Higher than usual concentrations of Sm, Eu, Tb, Dy, and Lu caused these two samples to be misclassified (as Millbrig) in the discriminant analysis, as shown on the classification diagram (fig. 12). The phosphorus concentrations of 0.14% and 0.17% P_2O_5 in these two samples are comparable to the $0.14\% \pm 0.08\%$ mean P_2O_5 content found in 27 other analyzed samples (table 3). Therefore, the high rare earth element concentrations probably are not related to greater amounts of apatite in these samples.

Variations in the concentrations of rubidium and cesium also exist in the Mississippi Valley. These elements are higher in the Deicke of Missouri than in the north. Ten Missouri samples with $7.7 \pm 1.5\%$ K_2O contained 120 ± 19 ppm rubidium and 20 ± 8 ppm cesium compared to 25 control group samples from the north that had 76 ± 12 ppm rubidium, 3.6 ± 2.0 ppm cesium, and $11.0 \pm 2.9\%$ K_2O . But the high potassium concentration of the control group samples reflects significant K-feldspar in those samples and, as already discussed, rubidium and cesium contents decrease as K-feldspar content increases in a sample. Therefore, the Missouri samples are more comparable to 15 northern Deicke samples with $8.1 \pm 1.0\%$ K_2O , 85 ± 12 ppm Rb, and 4.8 ± 1.9 ppm Cs. Thus, samples from Missouri that are rich in mixed-layer clays contained about 40% more rubidium and 4 times as much cesium as did similar samples from the northern outcrop area. Because subsequent chemical reactions would have erased the record of rubidium and cesium in the volcanic ash, the regional difference in these two elements is attributed to differences in diagenesis of the ash.

In parts of the northern outcrop area, the Deicke consists of very fine- to coarse-grained, brittle K-feldspar that commonly occurs as thin lenses within the K-bentonite. X-ray diffraction analysis shows it to be authigenic, monoclinic K-feldspar. (The formal stratigraphic name K-bentonite is applied to the bed even though at some localities it may consist primarily of K-feldspar.) The K-feldspar is particularly common in outcrops between the general vicinity of Dickeyville, Wisconsin, and Rochester, Minnesota. In this area the K-feldspar stands out when wet as a prominent grayish orange pink (5 YR 7/2) to light brown (5 YR 5/6) bed. In some outcrops, the K-bentonite grades laterally, within 1 or 2 m, to a soft, earthy mixture of clay and K-feldspar, then to hard, dense, very fine-grained K-feldspar. Weiss (1954) described similar "feldspathized" tuffs from the Wise Lake and Dubuque Formations (Galena Group) in southeastern Minnesota.

The mixed-layer illite/smectite assemblage characteristic of K-bentonites has a potassium content of up to 8% K_2O (Hower and Mowatt, 1966). Whole rock samples of the Deicke and other Decorah K-bentonites that contain more K_2O than this amount characteristically contain K-feldspar. Where the K_2O content is 13% to 14% or more (pure K-feldspar has 16.9% K_2O) the bed is generally indurated, but a few samples that had a K_2O content within this range are not indurated (e.g., MV6-1, 13.99% K_2O). Because these samples are not indurated, they are believed to contain more mixed-layer clay than do indurated samples with the same amount of K_2O . But because they have the same amount of K_2O , they must contain clay of higher potassium content (i.e., a high proportion of illite to smectite layers) than do the other samples. Some samples with significantly lower K_2O contents are indurated. These samples contain principally K-feldspar as opposed to mixed-layer clay, but they are diluted with calcite (e.g., MV11-1, 8.49% K_2O ; 22.8% CaO; 14.1% K_2O on a calcite-free basis). The occurrence of barium feldspar will also dilute the potassium level; only one indurated sample (unassigned Decorah K-bentonite sample DRK-224, 12.91% K_2O) had significant barium ($4.7 \pm 0.7\%$ Ba by INAA) in the feldspar. Detailed clay mineral studies of these samples are now in progress. The relationship between potassium content and the percentage of illite in the illite/smectite will be discussed in a separate paper.

K-feldspar is most abundant in the Deicke, Millbrig, and Elkport K-bentonites in northeastern Iowa and southwestern Wisconsin, and in the K-bentonite bed situated above the Millbrig in the Kings Lake Formation of east-central Missouri. In eastern Missouri, K-feldspar content decreases southward in both the Deicke and Millbrig Beds.

For three localities (21, 23, and 40) samples of the K-bentonite and associated K-feldspar were chemically analyzed. All of the samples were recognizable as the Deicke K-bentonite Bed on the basis of their chemical composition. For three other localities (17, 20, and 22)

where stratigraphic control is very good and the Deicke is entirely K-feldspar, the chemical analyses also gave a positive identification of the bed.

In the northern outcrop area, the Deicke is commonly 5 to 7 cm thick but varies from a trace to 10 cm (fig. 13). In the south it gradually thickens from less than 5 cm in western Illinois to more than 15 cm near Ste. Genevieve, Missouri. It is consistently present in outcrops of eastern Missouri, where it typically forms a prominent re-entrant between the limestones of the Platteville Group and Castlewood Limestone Member. Near Cape Girardeau (locality 66) the Deicke reaches its maximum thickness (approx-

mately 40 cm) in the Mississippi Valley. At this locality the K-bentonite is underlain by 1 to 2 cm of brownish gray (5 YR 4/1) to olive-black (5 Y 2/1) chert similar to that described by Miller and Fuller (1954) beneath certain thick K-bentonites in Virginia. The chert may have formed by replacement of the underlying limestone by silica freed during diagenetic alteration of the volcanic ash.

In southeastern Minnesota, the Deicke lies within the Carimona Limestone Member (fig. 14). Templeton and Willman (1963), however, assigned the basal part of the Carimona in southern Minnesota and all of it south of Decorah, Iowa, to the Castlewood Limestone Member. They judged the K-bentonite in the Carimona to be the Millbrig K-bentonite ("Spechts Ferry bentonite") and thought that the Deicke was absent. Kolata et al. (1983) showed in a preliminary investigation of chemical fingerprinting that this correlation was incorrect and that both the Deicke and Millbrig K-bentonites are widespread in the Decorah of Minnesota, a fact that was established by Sardeson (1928), Stauffer and Thiel (1941), Weiss and Bell (1956), and reconfirmed in this report. As correlated herein, all Carimona strata below the Deicke K-bentonite are older than the type Castlewood, whereas the upper part of the Carimona is approximately coeval with the Castlewood.

Templeton and Willman's (1963) miscorrelation of the K-bentonite beds is shown in their figure 22. At St. Paul and Rochester, Minnesota, they showed a K-bentonite at the base of the Glencoe Member of the Spechts Ferry Formation and one in the Garnaville Member of the Guttenberg Formation. On the basis of current nomenclature (Willman and Kolata, 1978) they would have considered these to be the Millbrig and Elkport, respectively. It is clear from chemical fingerprinting and physical tracing through numerous outcrops in Iowa and Minnesota that at the St. Paul and Rochester sections, the lower K-bentonite bed in their figure 22 is the Deicke and the upper is the Millbrig. Consequently, between Minnesota and Iowa they miscorrelated the Deicke with the Millbrig and the Millbrig with the Elkport. Cisne et al. (1984, p. 279, fig. 8), in their study of depth-related fossil assemblage gradients, accepted Templeton and Willman's K-bentonite correlation between the St. Paul and Guttenberg, Iowa, sections. In effect, Cisne et al. (1984) correlated the Deicke and Millbrig at St. Paul with what is now known to be the Millbrig and Elkport at Guttenberg. Complicating the matter is the fact that the Deicke is absent in the vicinity of Guttenberg.

In northeastern Iowa and parts of southwestern Wisconsin the Deicke lies on the McGregor Limestone of the Platteville Group. Near Dickeyville, Wisconsin, the Deicke lies on the thin western edge of the Quimbys Mill Formation (figs. 14 and 15). East of the Grant-Lafayette County line in Wisconsin and adjacent parts of northern Illinois, the Deicke pinches out. In western Illinois and eastern Missouri, the Deicke lies at the base of the Castlewood Member of the Spechts Ferry (fig. 16). Between Ste. Genevieve (lo-



Figure 13. Thickness of the Deicke K-bentonite Bed. Contour interval 5 cm; location of measured sections shown by small dots.

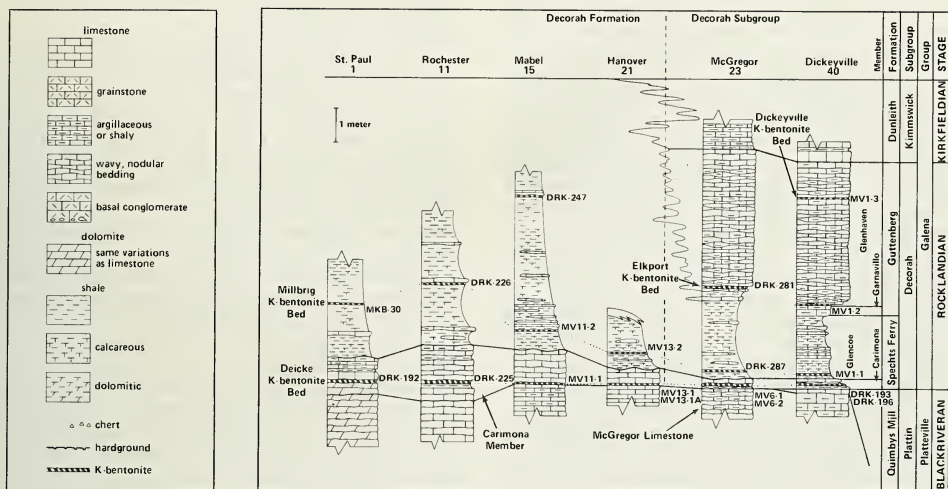


Figure 14. Correlation of Decorah K-bentonite beds at outcrops in southeastern Minnesota, northeastern Iowa, and southwestern Wisconsin. The distribution of localities is shown in figure 5. No horizontal scale.

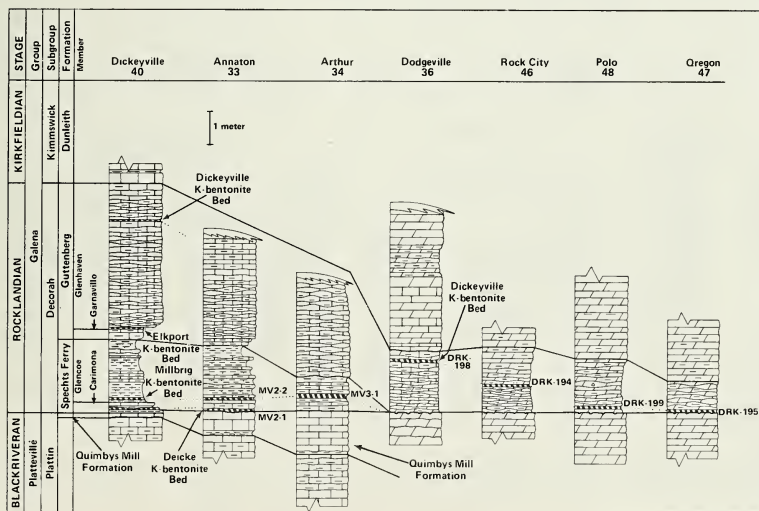


Figure 15. Correlation of Decorah K-bentonite beds at outcrops in southern Wisconsin and northern Illinois. The distribution of localities is shown in figure 5. No horizontal scale.

cality 65) and Cape Girardeau (locality 66), Missouri, the Decorah is poorly exposed and no K-bentonite samples were available. However, several geophysical logs from oil test wells were used to correlate the Decorah strata in this area. One of these is the Mississippi River Transmission Company No. 1 Meisner (fig. 17) in Perry County, Missouri (NW1/4 NW1/4 NE1/4 SE1/4 Sec. 2, T 34 N, R 13 E). The lateral log with gamma ray track shows interbedded shale and limestone of the Kings Lake Formation and Glencoe Shale Member of the Spechts Ferry Formation between 3,155 and 3,185 feet and the Castlewood Limestone Member between 3,183 and 3,200 feet. A prominent deflection at 3,200 feet may mark the Deicke K-bentonite Bed. This is supported by the presence of small fragments of K-bentonite with biotite flakes in the drill cuttings (Illinois State Geological Survey sample set 53784) from the interval 3,205 to 3,200 feet (Howard R. Schwalb, personal communication, 1983). Unfortunately, there was too little K-bentonite sample for a chemical analysis.

Another informative log was obtained from the Shell Oil Company No. 1 Trail of Tears State Park oil test in Cape Girardeau County, Missouri (SE1/4 SW1/4 NW1/4 NE1/4 Sec. 15, T 32 N, R 14 E). The sonic-gamma ray log shows shaly limestone of the Decorah Subgroup from 872 to 902 feet and the Castlewood Limestone Member from 902 to 926 feet. A prominent deflection in gamma ray intensity at 926 feet probably marks the position of the Deicke K-bentonite Bed. The stratigraphic succession

shown on this log is very similar to the section exposed 18 km south in Grays Point quarry (locality 66), near Ilmo, Missouri (fig. 16).

The most obvious change between the Ste. Genevieve outcrop and Grays Point quarry is the thickening of the Castlewood Limestone Member from 2 m in the north to 6 m in the south. This thickening is consistent with the overall thickening of the Platin (including the Castlewood Limestone Member) from a total of 90 m near Ste. Genevieve to 180 m at Grays Point quarry. On the basis of geophysical logs from western Kentucky, it appears that the Deicke is equivalent to the "Pencil Cave" (McFarlan, 1943) or T-3 (Wilson, 1949) K-bentonite of Kentucky and Tennessee (Kolata et al., 1984). However, more chemical analyses and detailed study of geophysical logs are necessary to substantiate this correlation.

Millbrig K-bentonite Bed

Like the Deicke, the Millbrig K-bentonite Bed has a consistent and diagnostic chemical composition that can be recognized from St. Paul, Minnesota, to Ste. Genevieve, Missouri. Samples of the Millbrig from Missouri are characterized by higher thorium and hafnium than the control group samples. This is the primary reason that the Missouri samples all plotted to the left of the control group centroid on the territorial map (fig. 12). Like the Deicke, the Millbrig in Missouri contains higher amounts of rubidium and cesium than are present in the northern outcrop

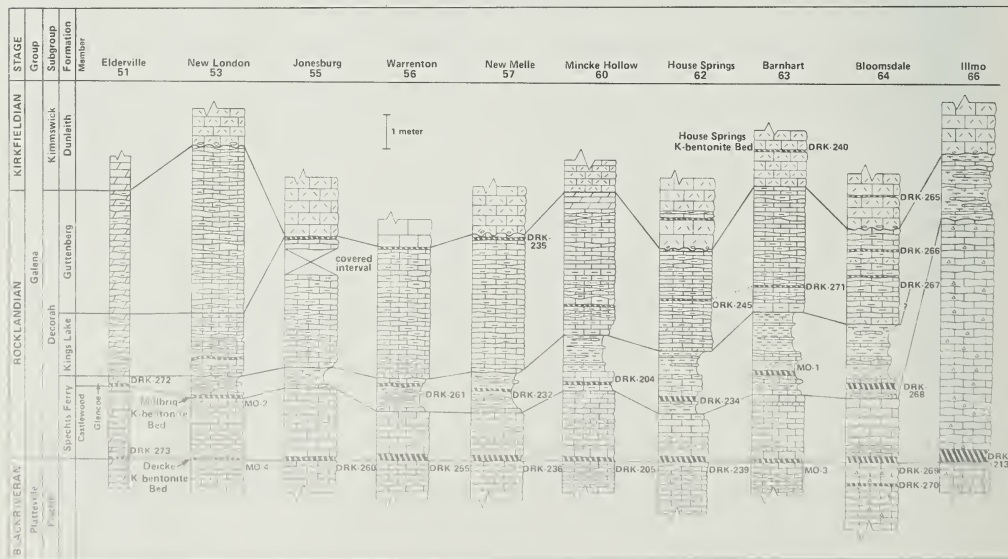


Figure 16. Correlation of Decorah K-bentonite beds in western Illinois and eastern Missouri. The distribution of localities is shown in figure 6. No horizontal scale.

area in samples with about the same mixed-layer clay content. Thirteen samples from the southern outcrop area had $8.2 \pm 1.9\%$ K₂O, 119 ± 25 ppm Rb, and 24 ± 11 ppm Cs, whereas a group of 23 northern samples had $8.2 \pm 1.1\%$ K₂O, 87 ± 10 ppm Rb, and 5.1 ± 1.2 ppm Cs.

Throughout most of the northern outcrop area, the Millbrig is generally 1 to 5 cm thick (fig. 18). It is absent in the vicinity of Cannon Falls, Minnesota (locality 7), and near Jonesburg, Missouri (locality 55). The Millbrig is present as far east as Mineral Point, Wisconsin (locality 35); thus, within the Mississippi Valley it extends about 25 km beyond the eastern limit of the Deicke. Near Platteville, Wisconsin (localities 33, 37, and 38), the Millbrig is between 12 and 15 cm thick, which is unusually thick for that area. In the southern outcrop area, it thickens southward from about 4 cm near Elderville, Illinois, to more than 15 cm around Ste. Genevieve, Missouri.

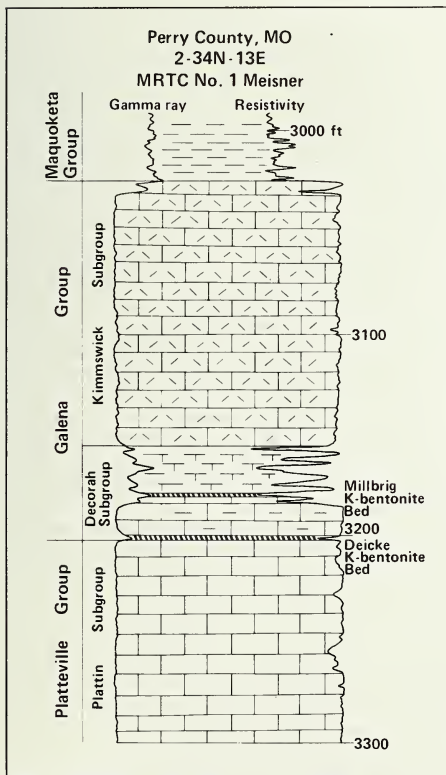


Figure 17. Gamma ray-resistivity log of the Mississippi River Transmission Co. No. 1 Meisner well in Perry County, Missouri. The log shows a prominent deflection at the Deicke and Millbrig K-bentonite Beds.

In southeastern Minnesota and northeastern Iowa, the Millbrig occurs in the lower part of the Decorah Formation (fig. 14). Near Galena, Illinois (locality 45), the southernmost exposure of the Millbrig in the northern outcrop area, the Deicke is absent and the Millbrig overlies 0.48 m of Carimona Limestone, which in turn overlies the Quimbys Mill Formation of the Platteville Group. At Elderville, Illinois (locality 51), the Millbrig lies within argillaceous dolomite of the Kings Lake Formation. Farther south at New London, Missouri (localities 52 and 53), it lies below about 30 cm of Glencoe Shale Member. Near Barnhart and Bloomsdale, Missouri (localities 63, 64, and 65), the

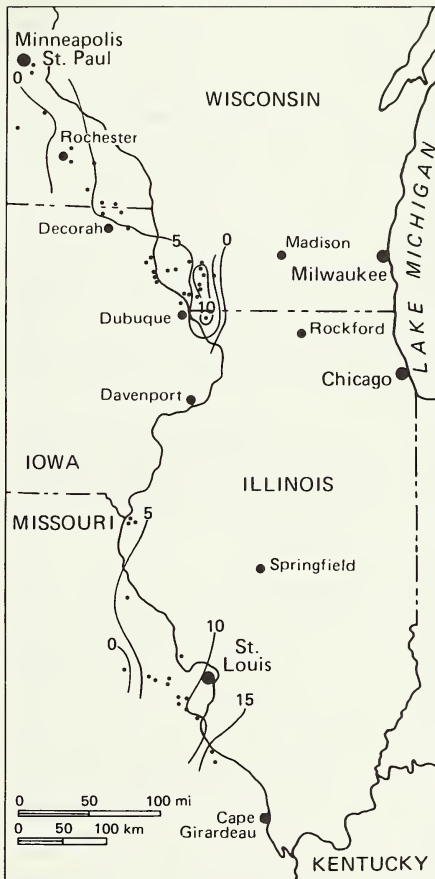


Figure 18. Thickness of the Millbrig K-bentonite Bed. Contour interval 5 cm; locations of measured sections shown by small dots.

Millbrig lies at the base of the Glencoe Shale. The Millbrig has not been identified positively in outcrop south of locality 65. Its position within the stratigraphic succession suggests that it may be equivalent to the "Mud Cave" (McFarlan, 1943) or T-4 (Wilson, 1949) K-bentonite of Kentucky and Tennessee (Kolata et al., 1984). More information is needed, however, to confirm this correlation.

Elkport K-bentonite Bed

The Elkport can be identified by chemical fingerprinting in a limited area of the northern outcrop area between McGregor, Iowa, and Galena, Illinois (fig. 5). It is a 1 to 5 cm bed that occurs at the conspicuous re-entrant between the Glenhaven and Garnaville Members of the Guttenberg Formation. The bed lies about 2 to 2.5 m above the Millbrig K-bentonite Bed.

In addition to the six samples used in the control group, two others (DRK-252 and -285; table 2) were analyzed and the data treated statistically. They classified correctly as the Elkport K-bentonite in the discriminant analysis, but in the plot of the scores on only the first two discriminant functions (fig. 12) DRK-285, which was collected 2 m above the Millbrig K-bentonite near Potosi, Wisconsin (locality 41), does not fall in the Elkport field. On the basis of its stratigraphic occurrence there is no doubt that it was collected from the Elkport K-bentonite. The potassium content of this sample is 10.75% K_2O , which is significantly higher than the mean ($9.2\% \pm 0.7\%$) of the six control group samples. This sample contains enough K-feldspar to lower the concentrations of scandium, thorium, and other key discriminating elements that are negatively correlated with potassium content (fig. 10), so that this sample is at the edge of the range of chemistry displayed by the Elkport reference samples, and is plotted to the left of the reference group in figure 12. The behavior of this sample illustrates the fact that the group of samples used for the control group for a K-bentonite bed must adequately represent the bed.

Dickeyville K-bentonite Bed

The Dickeyville K-bentonite Bed has been identified by chemical fingerprinting at five localities in southern Wisconsin and northern Illinois (fig. 5). At its type section (locality 40) in southwestern Wisconsin, the Dickeyville is in the upper part of the Guttenberg Formation approximately 5 m above the Millbrig K-bentonite. East and south of there the Spechts Ferry Formation gradually pinches out and the Guttenberg Formation decreases in thickness from the base up (fig. 15). Near Dodgeville, Wisconsin (locality 36), the K-bentonite is 1.5 m above the Quimbys Mill Formation (Platteville Group). To the southeast at Rock City, Polo, and Oregon, Illinois (localities 46, 47, and 48), the interval decreases to 0.8, 0.09, and 0 m, respectively. The gradual decrease from northwest to southeast of the interval between the Dickeyville K-bentonite and

the top of the Platteville Group clearly shows the overlapping nature of the Decorah Subgroup. Thinning of the Decorah in south-central Wisconsin and north-central Illinois suggests that this area, situated at the southern end of the Wisconsin Arch, was uplifted at the end of Blackriverian time and was gradually overlapped by Decorah rocks in Rocklandian time.

Unassigned Decorah K-bentonite beds

Near Mabel, Minnesota (locality 15), a 2 cm thick K-bentonite bed occurs beneath a layer of fossiliferous limestone in the Decorah Shale 4 m above the Millbrig K-bentonite (fig. 14). Its stratigraphic position suggests that it could be either the Elkport or Dickeyville K-bentonite Bed. Chemical analysis of a sample (DRK-247) from this locality showed that it differs from these two beds in having lower concentrations of the heavy rare earth elements and thorium (table 2). On the basis of sodium content ($Na_2O = 0.078\%$), the bed is most like the Elkport. Values for Sc, Zr, Ti, Hf, and Ta are similar to values for those elements in either the Elkport or Dickeyville. The bed does not have a distinct chemical fingerprint that would allow a confident correlation with either the Elkport or Dickeyville.

In the southern outcrop area there are at least two K-bentonite and/or K-feldspar beds in the Decorah Subgroup above the Millbrig K-bentonite Bed (fig. 16). The lowermost bed is 0.5 to 3 cm thick and occurs in the Kings Lake Formation approximately 1 to 3 m above the Millbrig; samples of the bed from localities 52, 53, 60, 62, and 63 were analyzed. At several other localities the horizon is marked only by a prominent shaly bedding plane. This appears to be the K-bentonite noted by Templeton and Willman (1963, p. 111) in the Kings Lake Formation. Its stratigraphic position suggests a possible correlation with the Elkport K-bentonite. Samples were fairly consistent in their chemistry, given the fact that they are contaminated to some degree with limestone and shale. Their chemistry, however, is not the same as that of the six Elkport reference samples from the northern outcrop area. Potassium in the Missouri bed, largely K-feldspar, ranged from 9.4% to 15.5% K_2O , and averaged 11.9%. One sample, DRK-222 (locality 53), was unusually high in calcite ($CaO = 16.6\%$). Its K_2O content of 10.13% was calculated to be 14.2% on a calcite-free basis. With regard to the good discriminating elements, these samples are lower in Sc, Zr, Hf, Ta, Dy, Yb, Lu, and Th, but higher in Ti. With the exception of titanium, these lower concentrations are expected for samples with so much more K-feldspar than is present in samples with an average potassium concentration of 9.2% K_2O , which we have in the Elkport control group. Sodium content and the Hf/Ta ratio would not be expected to change significantly with increasing K-feldspar content, and these two parameters for the Missouri samples match the Elkport in the north. Because we do not have Elkport samples with high K-feldspar content in the north

where the stratigraphy for that bed is well known, we cannot demonstrate that the chemistry of the samples in Missouri is consistent with that of the Elkport in the north, even allowing for changes due to feldspathization.

Another bed of K-bentonite and K-feldspar up to 6 cm thick occurs in the Guttenberg Formation 2 m below the Dunleith Formation at locality 54 and at or near the top of the Kings Lake Formation at localities 55, 56, 57, and 58 (fig. 16). Its position in the stratigraphic succession suggests a possible correlation with the Dickeyville K-bentonite of the northern outcrop area.

Compared to the Dickeyville, or the Elkport for that matter, samples from this bed have similar levels of Sc, Zr, and Hf, higher levels of Ti, and lower levels of Ta, Th, and heavy rare earth elements. Sodium values for three samples (DRK-235, -238, and -243) range from 0.047% to 0.081% Na₂O, which is closer to the range for the Elkport. The concentrations of sodium and titanium may be influenced by admixing of shale.

Farther south near Bloomsdale, Missouri (locality 64), the Kings Lake Formation contains two K-bentonite beds (samples DRK-266 and -267) about 1 m apart (fig. 16). One of the two beds is probably equivalent to a K-bentonite bed (sample DRK-210) in the upper part of the Kings Lake 14 km southeast at locality 65. These beds are chemically similar to the K-bentonite/K-feldspar bed discussed in the preceding paragraphs. They are particularly alike in their relatively high iron and titanium and low tantalum values.

In summary, because we had so few samples of the Decorah K-bentonites above the Millbrig in the southern outcrop area, it was difficult to correlate these beds throughout their outcrop area and particularly with the Elkport and Dickeyville K-bentonites of the northern outcrop area. Contributing to the problem is the fact that these beds are thin, impure, and locally discontinuous. In addition, there may be a gradational change in chemical composition from the northern outcrop area to the southern. Furthermore, we did not have a sufficient number of Elkport and Dickeyville samples in the control group to define the chemistry of those two beds with the desired statistical confidence. Because of these problems and uncertainties, we choose not to extend the Elkport and Dickeyville nomenclature into the southern outcrop area.

Other K-bentonite beds

Two non-Decorah K-bentonite beds were noted during this investigation. One of these occurs approximately 1 m above the Kings Lake Formation in the Kimmiswick Subgroup (Dunleith Limestone) at several localities (59, 61, 62, 63, and 64) in eastern Missouri (fig. 16). The bed is herein named the House Springs K-bentonite Bed after the town of House Springs, Jefferson County, Missouri, which is 0.8 km south of the type section (locality 62; figs. 4 and 16). The other bed is in the Platteville Group, 0.6 m below

the Deicke K-bentonite at a single locality near Bloomsdale, Missouri (locality 64; fig. 16). The beds are discussed here because of their proximity in the stratigraphic succession to the Decorah K-bentonites.

The House Springs K-bentonite is a 1 to 3 cm thick bed that is commonly overlain by about 15 cm of argillaceous limestone. Analyses of three samples (DRK-218, -240, and -265) showed the bed to have low titanium ($\text{TiO}_2 = 0.23\%$ to 0.25%) and high tantalum (2.1 to 2.3 ppm) levels (table 2). The samples also had similar concentrations of zirconium (252 to 314 ppm) and hafnium (12 to 14 ppm). On the basis of these 4 elements, the samples would be classified as belonging to the same K-bentonite bed. However, sample DRK-265 is somewhat anomalous chemically because it has very high arsenic (160 ppm) and antimony (2.8 ppm) concentrations. In addition, it has appreciably higher levels of rare earth elements than do samples DRK-218 and -240. For example, its dysprosium content is 7.6 ppm compared with 1.7 and 2.2 ppm in the other two samples. Like other K-bentonite beds in Missouri, these three samples have high rubidium (120, 140, and 150 ppm) and cesium (22, 29, and 32 ppm) concentrations.

Near Bloomsdale, Missouri (locality 64), two K-bentonite beds occur in the 2.5 m interval below the Millbrig K-bentonite (fig. 16). The upper 15 cm thick bed (sample DRK-269) was identified chemically as the Deicke. The lower bed (sample DRK-270) is 1 to 3 cm thick, and is characterized by low Ti, Zr, and rare earth elements, and high Ta. Chemically, this bed is much like the Millbrig K-bentonite.

STRATIGRAPHIC RELATIONSHIPS OF THE DECORAH SUBGROUP

The K-bentonite beds are useful time-stratigraphic markers that greatly facilitate correlation of Decorah strata in the Mississippi Valley. Figure 19 shows the stratigraphic relationships of the Decorah Subgroup and adjacent rocks along a transect from St. Paul, Minnesota, to Bloomsdale, Missouri. Most data used to construct the cross section were from the northern and southern outcrop areas. Interpretation of stratigraphy between northwestern Illinois and northeastern Missouri was based on limited subsurface information.

The Deicke and Millbrig K-bentonite Beds tie the northern and southern sections together. The remarkably uniform lithology between these two K-bentonites throughout most of the Mississippi Valley, consisting of approximately 2 m of shale and limestone, indicates widespread uniformity of depositional rates and sedimentary environment. An exception to this uniformity occurs in parts of northeastern Iowa and southwestern Wisconsin where the two K-bentonites converge. At some localities between Clayton and Guttenberg, Iowa, the Deicke is absent. Scour marks on top of the Carimona Limestone Member

within the area (localities 15, 16, 20, 21, and 23) suggest that a part of the interval, in places including the Deicke, was removed by erosion prior to deposition of the Millbrig K-bentonite. The erosion may have been caused by localized uplift during Rocklandian time. Toward the south the interval gradually increases to about 2.5 m near Barnhardt, Missouri. Data are sparse southeast of Bloomdsdale, Missouri, but certain geophysical logs from southeastern Missouri and southern Illinois suggest that the interval increases to about 6 or 7 m. Thickening of the Castlewood Limestone Member accounts for most of the increased section.

The Castlewood has been assigned by some authors (Grohskopf, 1948; Herbert, 1949; Howe, 1961; Larson, 1951) to the Platin Subgroup (Platteville Group) because of the lithologic similarity of the two units. Grohskopf (1948) judged that the contact between the Decorah shale and Platin limestone (including the Castlewood) is disconformable in eastern Missouri. Zoning of the Platin based on lithology and insoluble residues led him to believe that the Decorah (Glencoe Shale Member) overlaps older beds from the southeast to the northwest. If a disconformity exists in this area, it must lie below the Castlewood Limestone Member and the Deicke K-bentonite Bed because these units can be traced in outcrop and subsurface along a transect that for the most part coincides with that of Grohskopf (1948, p. 353, fig. 1). In this area the Glen-

coe Shale is conformable with the underlying Castlewood Limestone. If a disconformity does exist below the Castlewood, it would emphasize the closer relationship of the Castlewood Limestone to the Decorah rather than to the Platin.

The occurrence of the Millbrig K-bentonite at the base of the Kings Lake Formation in Hancock County, Illinois (localities 49, 50, 51), indicates that the Kings Lake is, at least in part, coeval with the Glencoe Shale Member (fig. 19). The absence of Kings Lake strata in the northern outcrop area led Herbert (1949) and Templeton and Willman (1963) to speculate that an unconformity is present at the base of the Guttenberg Formation in the north. It seems more likely, however, that the Kings Lake is a silty carbonate facies of the Spechts Ferry and Guttenberg Formations. In view of the available evidence, the stratigraphic relations of the Decorah units shown in figure 18 of Templeton and Willman (1963) are incorrect. The time relations established by the K-bentonite beds indicate that the stratigraphic units are in part laterally gradational rather than stacked in a layer-cake fashion.

From New London southward to Ilmo, Missouri, the contact between the Decorah and the overlying Kimmswick Subgroup (Dunleith Formation) is an unconformity marked by a sharp lithologic change (fig. 19). The Kimmswick overlaps several Decorah formations within this area. It overlies the Guttenberg Formation as far south as Batch-

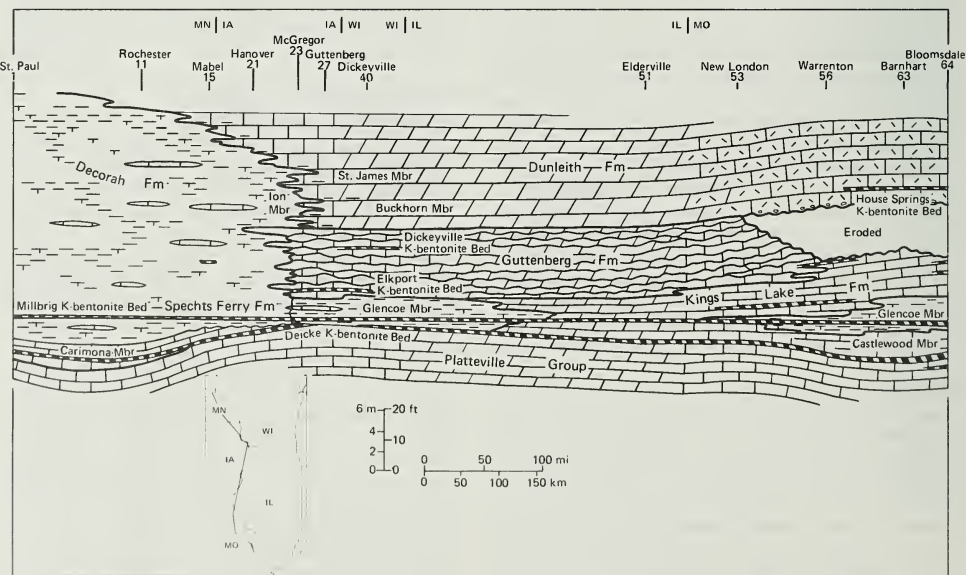


Figure 19. Diagrammatic cross section of Decorah and adjacent strata from St. Paul, Minnesota, to Bloomsdale, Missouri. The various lithologic units are intertongued; however, in practice the formal lithostratigraphic boundaries should be marked by vertical cutoffs.

town, Illinois, the Kings Lake Formation at least as far southeast as Ste. Genevieve, Missouri, and 2 m of interbedded greenish gray shale and very fossiliferous limestone at Illmo (fig. 16). In places the basal Kimmswick contains a pebble conglomerate formed from fragments of the underlying formations. The conglomerate marks a period of erosion, perhaps related to uplift of the Ozark Dome during Rocklandian time. The Kimmswick apparently overlapped a relatively flat surface because the interval between the top of the Kings Lake and the overlying House Springs K-bentonite Bed is consistently about 1 m thick from near Eureka (locality 59) to Bloomsdale, Missouri (locality 64), a distance of about 65 km.

SUMMARY

- The Deicke, Millbrig, Elkport, and Dickeyville K-bentonite Beds of the Decorah Subgroup each have a unique chemical fingerprint. The chemical signatures of the Deicke and Millbrig can be recognized in outcrop and subsurface from southern Minnesota to southeastern Missouri, a distance of about 900 km. The Elkport and Dickeyville are chemically identifiable only in the northern outcrop area of the Mississippi Valley. Two K-bentonite beds occur in places above the Millbrig K-bentonite in eastern Missouri, but the chemical data are too inconclusive to assign them to any formally named beds.

- Because of their wide distribution and distinctive chemistry, these K-bentonite beds provide valuable time-parallel stratigraphic markers that facilitate the correlation of the Decorah rocks in the Mississippi Valley region and possibly beyond. The correlations indicate that some Decorah units are lithologically uniform over wide areas but others vary laterally.

- Fingerprinting of the K-bentonites was accomplished through instrumental neutron activation and X-ray fluores-

cence analyses for 26 elements followed by stepwise discriminant analysis. Multivariate statistical analysis of such a large number of chemical variables provides a powerful tool for discriminating geochemical differences among the Decorah K-bentonite beds and for the identification of unknown samples.

- The elements that serve as the best discriminators of chemical composition between K-bentonite beds are Na, Sc, Ti, Zr, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, and Th. These are the elements with different average concentrations from bed to bed and relatively a small range of concentration within beds.

- The Deicke and Millbrig K-bentonite Beds show an increase in hafnium, thorium, and the rare earth elements from north to south. The increase is not enough to obscure the chemical fingerprint, but it does indicate that variations in composition exist over long distances. As these beds are traced toward their source area in the southeastern states, variations in the concentration of certain elements should be expected.

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APPENDIX: LOCALITY REGISTER

K-bentonite samples were collected from the Decorah Subgroup at the following 67 localities. The asterisks mark the localities where the control group samples were obtained. Some localities listed include the stratigraphic occurrence for samples that were not assigned to a formally named K-bentonite bed. Figures 5 and 6 show the distribution of localities and the K-bentonite beds that are present. Table 2 lists all samples tested and the localities where they were collected.

* 1. St. Paul (Summit Avenue) Section—exposure in bluff of Mississippi River at end of Summit Avenue in St. Paul, Ramsey Co., MN (E½ NE¼ SW¼ Sec. 5, T 28 N, R 23 W, St. Paul West 7.5-minute Quad.). Deicke and Millbrig.

* 2. Twin City Brick and Tile Company Section—Twin City Brick and Tile Company pit at Cherokee Heights, St. Paul, Ramsey Co., MN (SW¼ SE¼ SE¼ Sec. 12, T 28 N, R 23 W; St. Paul East 7.5-minute Quad.). Millbrig.

- * 3. Faribault East Section—quarry on south side of Straight River, 1.2 km east of Faribault, Rice Co., MN (SW¼ SW¼ SE¼ Sec. 33, T 110 N, R 20 W; Cannon City 7.5-minute Quad.). Deicke.
- * 4. Wangs Northwest Section—roadcut on State Highway 56, 3.2 km northwest of Wangs, Goodhue Co., MN (center S½ Sec. 16, T 111 N, R 18 W, Sogn 7.5-minute Quad.). Deicke.
- * 5. Sogn Section—roadcut on highway 14 just south of intersection with highway 9 near Sogn, Goodhue Co., MN (NW¼ SE¼ Sec. 24, T 111 N, R 18 W; Sogn 7.5-minute Quad.). Deicke.
- 6. Sogn South Section—roadcut near intersection of highways 14 and 44, 5 km south of Sogn, Goodhue Co., MN (SW¼ Sec. 1, T 110 N, R 18 W, Kenyon 7.5-minute Quad.). Deicke.
- * 7. Cannon Falls Southeast Section—quarry on north side of highway 25, 0.7 km southeast of Cannon Falls, Goodhue Co., MN (SE¼ SE¼ SE¼ Sec. 18, T 112 N, R 17 W; Cannon Falls 7.5-minute Quad.). Deicke.
- 8. Danesville Southeast Section—quarry on north side of highway 5, 2.7 km southeast of Danesville, Olmsted Co., MN (Center S½ NE¼ Sec. 18, T 107 N, R 15 W, Byron 7.5-minute Quad.). Deicke.
- 9. Rochester North Section—quarry on east side of U.S. Highway 63 on north side of Rochester, Olmsted Co., MN (SE¼ SW¼ Sec. 24, T 107 N, R 14 W, Rochester 7.5-minute Quad.). Millbrig.
- * 10. Rochester South Section (Golden Hill)—roadcut on U.S. Highway 52 in Golden Hill suburb on southwest side of Rochester, Olmsted Co., MN (SE¼ NE¼ NE¼ Sec. 15, T 106 N, R 14 W; Simpson 7.5-minute Quad.). Deicke.
- * 11. Rochester Southeast Section—quarry on old U.S. Highway 52 (Marion Road) on southeast side of Rochester, Olmsted Co., MN (SW¼ SE¼ NE¼ Sec. 21, T 106 N, R 13 W; Simpson 7.5-minute Quad.). Deicke and Millbrig.
- * 12. Cummingsville Section—roadcut on State Highway 30, 1.2 km west of Cummingsville, Olmsted Co., MN (NW¼ SE¼ NW¼ Sec. 28, T 105 N, R 12 W; Washington 7.5-minute Quad.). Deicke.
- * 13. St. Charles South Section—quarry on west side of State Highway 74, 1.8 km south of Interstate Highway 90 and 2.8 km south of St. Charles, Winona Co., MN (NW¼ SE¼ SE¼ Sec. 31, T 106 N, R 10 W; St. Charles 7.5-minute Quad.). Deicke and Millbrig.
- * 14. Preston, MN, West Sections—roadcuts and quarry on highway 12, 9.4 km and 10.4 km, respectively, southeast of Preston, Fillmore Co., MN (NE¼ Sec. 7, T 102 N, R 9 W; and SW¼ Sec. 8, T 102 N, R 9 W; Lanesboro 7.5-minute Quad.). Deicke and Millbrig.
- * 15. Mabel Northwest Quarry—quarry on north side of county road, 0.4 km west of Minnesota State Route 43 and 2 km north of Mabel, Fillmore Co., MN (SE¼ SW¼ SE¼ Sec. 15, T 101 N, R 8 W, Mabel 7.5-minute Quad.). Deicke and Millbrig; DRK-247, Decorah Formation, 4 m above Millbrig K-bentonite.
- * 16. Spring Grove West Section—quarry on north side of State Highway 44, 5 km west of Spring Grove, Houston Co., MN (SE¼ SW¼ SE¼ Sec. 17, T 101 N, R 7 W, Spring Grove 7.5-minute Quad.). Deicke and Millbrig.
- * 17. Locust Northwest Section—quarry on east side of county road on the Hanson farm, 4 km northwest of Locust, Winneshiek Co., IA (NW¼ NW¼ SE¼ Sec. 26, T 100 N, R 8 W; Decorah 30-minute Quad.). Deicke K-feldspar and Millbrig.
- * 18. Ice Cave Section—roadcut on north side of Quarry Street, 0.4 km east of Ice Cave on north side of Decorah, Winneshiek Co., IA (NE¼ NW¼ NW¼ Sec. 15, T 98 N, R 8 W; Decorah 30-minute Quad.). Deicke.
- * 19. Decorah East Section—excavation near bridge on west side of Trout Run Creek on State Highway 9, 0.8 km east of Decorah, Winneshiek Co., IA (SW¼ NW¼ SW¼ Sec. 23, T 98 N, R 8 W; Decorah 30-minute Quad.). Deicke.
- * 20. Dorchester West Section—quarry 0.8 km south of State Highway 119, 7 km west of Dorchester, Allamakee Co., IA (SE¼ SW¼ SE¼ Sec. 17, T 100 N, R 6 W; Dorchester 7.5-minute Quad.). Deicke K-feldspar and Millbrig.
- * 21. Hanover East Section—quarry on east side of county road, 2 km east of Hanover, Allamakee Co., IA (NW¼ NW¼ SE¼ Sec. 25, T 99 N, R 6 W; Waukon 7.5-minute Quad.). Deicke K-bentonite and K-feldspar and Millbrig.
- * 22. Volney Section—roadcut 1.2 km north of Volney, Allamakee Co., IA (SW¼ NE¼ SE¼ Sec. 12, T 96 N, R 5 W; Waterville 7.5-minute Quad.). Deicke K-feldspar.
- * 23. McGregor South Section—quarry on east side of State Highway 340, 1.2 km south of intersection of highways 340 and 18 in McGregor, Clayton Co., IA (SW¼ SW¼ SE¼ Sec. 27, T 95 N, R 3 W; Prairie du Chien 15-minute Quad.). Deicke K-bentonite and K-feldspar, Millbrig, and Elkport.
- * 24. McGregor Southwest Section—cut along ditch on south side of county road X-50, 4 km southwest of McGregor, Clayton Co., IA (NW¼ NW¼ SE¼ Sec. 5, T 94 N, R 3 W; Clayton 7.5-minute Quad.). Deicke and Millbrig.
- * 25. Pattison Hill Roadcut—Pattison Hill roadcut, 0.4 km south of Clayton, Clayton Co., IA (SE¼ NW¼ SW¼ Sec. 1, T 93 N, R 3 W; Clayton 7.5-minute Quad.). Millbrig and Elkport.
- * 26. Guttenberg (X-56) Section—roadcut on west side of Hwy. X-56 ascending hill, 3.2 km north of Guttenberg, Clayton Co., IA (SE¼ NW¼ NW¼ Sec. 32, T 93 N, R 2 W; Guttenberg 7.5-minute Quad.). Elkport.

- *27. Guttenberg North Section—roadcut of U.S. Highway 52 where it ascends to the upland from the Mississippi River bottomland on the northwest side of Guttenberg, Clayton Co., IA (SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 5, T 92 N, R 2 W; Guttenberg 7.5-minute Quad.). Millbrig and Elkport (type section of the latter).
- *28. Guttenberg South Section—excavation 100 m west of U.S. Highway 52 on south side of Guttenberg, Clayton Co., IA (NE $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 29, T 92 N, R 2 W; Guttenberg 7.5-minute Quad.). Millbrig.
- *29. Beetown Northwest Section—quarry on north side of State Highway 35, 4 km northeast of Beetown, Grant Co., WI (SE $\frac{1}{4}$ NE $\frac{1}{4}$ NW $\frac{1}{4}$ Sec. 16, T 4 N, R 4 W; Hurricane 7.5-minute Quad.). Deicke and Millbrig.
- *30. Lancaster West Section—roadcut on County Road A, 6 km west of intersection of A with U.S. Highway 61 in Lancaster, Grant Co., WI (SW $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 31, T 5 N, R 4 W; Hurricane 7.5-minute Quad.). Deicke and Millbrig.
- *31. Fennimore West Section—roadcut on U.S. Highway 18, 5.1 km west of Fennimore, Grant Co., WI (NW $\frac{1}{4}$ NE $\frac{1}{4}$ NW $\frac{1}{4}$ Sec. 22, T 6 N, R 3 W; Fennimore 7.5-minute Quad.). Deicke and Millbrig.
32. Preston, WI, Southeast Section—quarry in valley of Platte River, north side of Ebenezer Road, 3.4 km southeast of Preston, Grant Co., WI (SW $\frac{1}{4}$ SW $\frac{1}{4}$ NE $\frac{1}{4}$ Sec. 32, T 6 N, R 1 W; Stitzer 7.5-minute Quad.). Millbrig.
- *33. Anneton South Section—quarry on west side of county road, 6 km south of Anneton, Grant Co., WI (SE $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 25, T 5 N, R 2 W; Ellenboro 7.5-minute Quad.). Deicke and Millbrig.
- *34. Arthur Section—quarry in back of the Boulder Lounge on northwest side of intersection of State Highway 80 and County Road A in Arthur, Grant Co., WI (NE $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 2, T 4 N, R 1 W; Rewey 7.5-minute Quad.). Millbrig.
- *35. Mineral Point Southwest Section—roadcut on U.S. Highway 151, 4.8 km southwest of Mineral Point, Iowa Co., WI (SE $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 10, T 4 N, R 2 E; Mineral Point 7.5-minute Quad.). Millbrig.
- *36. Dodgeville East Section—roadcut on north side of U.S. Highway 18, 5 km east of intersection of highways 18 and 23, Dodgeville, Iowa Co., WI (NE $\frac{1}{4}$ NW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 19, T 6 N, R 4 E; Jonesdale 7.5-minute Quad.). Dickeyville.
37. Platteville West Section (County Road B)—quarry on north side of County Road B along Young Branch of Platte River, 4 km west of Platteville, Grant Co., WI (NE $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 7, T 3 N, R 1 W; Dickeyville 7.5-minute Quad.). Millbrig.
38. Platteville West Section—small quarry on east side of road 4.5 km west of Platteville, Grant Co., WI (SW $\frac{1}{4}$ Sec. 18, T 3 N, R 1 W; Ellenboro 7.5-minute Quad.). Millbrig.
39. Dickeyville North Section—quarry on west side of road, 1.1 km north of U.S. Highway 151 and 4.8 km north-northeast of Dickeyville, Grant Co., WI (SW $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 2, T 2 N, R 2 W; Dickeyville 7.5-minute Quad.). Millbrig.
- *40. Dickeyville Northwest Section—quarry and roadcuts along U.S. Highway 61, 6.4 km northwest of Dickeyville, Grant Co., WI (NE $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 7 and S $\frac{1}{2}$ NW $\frac{1}{4}$ Sec. 7, T 2 N, R 2 W; Potosi 7.5-minute Quad.). Deicke K-bentonite and K-feldspar, Millbrig, Elkport, and Dickeyville (type section of the latter).
- *41. Potosi Southwest Section—road grade along steep bluff on northwest side of State Highway 133, 2.2 km southwest of Potosi, Grant Co., WI (NE $\frac{1}{4}$ NW $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 4, T 2 N, R 3 W; Potosi 7.5-minute Quad.). Deicke, Millbrig, and Elkport.
42. Boice Creek Section—outcrop along Boice Creek, 6.4 km west of Rockville, Grant Co., WI (SE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 17, T 3 N, R 3 W; Balltown 7.5-minute Quad.). Deicke and Elkport.
- *43. Spechts Ferry Section—ravine in high bluff south of Chicago, Milwaukee, St. Paul, and Pacific Railroad, 200 m east of Spechts Ferry, Dubuque Co., IA (SE $\frac{1}{4}$ SW $\frac{1}{4}$ NE $\frac{1}{4}$ Sec. 4, T 90 N, R 2 E; Potosi 7.5-minute Quad.). Elkport.
44. Sageville North Section—quarry in bluff west of Chicago, Milwaukee, St. Paul, and Pacific Railroad, 5.8 km north of Sageville, Dubuque Co., IA (NE $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 10, T 90 N, R 2 E; Dubuque North 7.5-minute Quad.). Millbrig.
- *45. Millbrig Southeast Section—cutbank along east side of Galena River, 1.6 km southeast of Millbrig, Jo Daviess Co., IL (near center Sec. 34, T 29 N, R 1 E, Galena 7.5-minute Quad.). Millbrig type section.
- *46. Rock City East Section—quarry 0.4 km south of State Highway 75, 0.8 km east of Rock City, Stephenson Co., IL (SE $\frac{1}{4}$ SW $\frac{1}{4}$ NW $\frac{1}{4}$ Sec. 22, T 28 N, R 9 E; Pecatonica 15-minute Quad.). Dickeyville.
- *47. Oregon East Section—quarry on Thorpe farm on north side of State Highway 64 on east side of Oregon, Ogle Co., IL (elongate section, 660 m from west line and 1320 m from south line, Sec. 2, T 23 N, R 10 E; Oregon 15-minute Quad.). Dickeyville.
- *48. Polo West Section—quarry along the Burlington Northern Railroad 1.6 km west of Polo, Ogle Co., IL (SE $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$ Sec. 18, T 23 N, R 8 E, Sterling 15-minute Quad.). Dickeyville.
49. New Jersey Zinc-Koefer Core—core (Illinois State Geological Survey G-7607), New Jersey Zinc Co. H-2, Koefer, 4 km southeast of Warsaw, Hancock Co., IL (NW $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 13, T 4 N, R 9 W; Warsaw 7.5-minute Quad.). Millbrig.
50. New Jersey Zinc-Bruder Well—core (Illinois State Geological Survey G-7883), New Jersey Zinc Co. H-3, Bruder, 4.5 km southeast of Warsaw, Hancock Co., IL (NE $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 23, T 4 N, R 9 W; Warsaw 7.5-minute Quad.). Deicke and Millbrig.

51. Elderville Section—New Jersey Zinc Co. H-1, R. Cochran, 3.6 cm (1 7/16 inch) core (Illinois State Geological Survey C-7838) drilled at elevation 669 feet, 1.5 km west of Elderville, Hancock Co., IL (NE¼ SW¼ SW¼ Sec. 15, T 4 N, R 8 W; Sutter 7.5-minute Quad.). Deicke and Millbrig.
52. New London North Section—outcrop on access road on west side of U.S. Highway 61, immediately south of bridge over Salt River, 2 km north of New London, Ralls Co., MO (NW¼ SW¼ NE¼ Sec. 36, T 56 N, R 5 W; Hannibal 15-minute Quad.). Millbrig; DRK-217, -223, and -224, Kings Lake Formation, 1 m above Millbrig K-bentonite.
53. New London Southeast Section—roadcut on U.S. Highway 61, 6.4 km southeast of New London, Ralls Co., MO (SE¼ NE¼ SE¼ Sec. 21, T 55 N, R 4 W; Hannibal 15-minute Quad.). Deicke and Millbrig; DRK-222, Kings Lake Formation, 1 m above Millbrig K-bentonite.
54. Batchtown South Section—roadcut on West Point Ferry Road, 3.6 km south of Batchtown, Calhoun Co., IL (SW¼ NW¼ SE¼ Sec. 20, T 7 N, R 2 W; Hardin 15-minute Quad.). Millbrig; DRK-243, Guttenberg Formation, 2 m below Dunleith Formation.
55. Jonesburg Southwest Section—quarry on Harold Casper farm in northern Warren County along Millam Creek, 3.7 km west-southwest of Jonesburg, Montgomery Co., MO (SW¼ NW¼ NW¼ Sec. 15, T 47 N, R 4 W; Jonesburg 7.5-minute Quad.). Deicke.
56. Warrenton Section—Missouri Limestone Company quarry, 6.4 km southeast of Warrenton, Warren Co., MO (SE¼ NE¼ NE¼ Sec. 15, T 46 N, R 2 W; Wright City 7.5-minute Quad.). Deicke and Millbrig.
57. New Melle Quarry Section—Joerling Bros. quarry on west side of highway F, 3.2 km south of New Melle, St. Louis Co., MO (SW¼ SW¼ SW¼ Sec. 2, T 45 N, R 1 E; New Melle 7.5-minute Quad.). Deicke and Millbrig; DRK-235, top of Kings Lake Formation.
58. New Melle Creek Section—outcrop in tributary of Callaway Fork on east side of highway F and beneath bridge with tributary crossing to west side of road, 1.3 km south of New Melle, St. Charles Co., MO (SE¼ NW¼ SW¼ Sec. 35, T 46 N, R 1 E; New Melle 7.5-minute Quad.). Deicke and Millbrig; DRK-238, Kings Lake Formation, 0.5 m below Dunleith Formation.
59. Eureka North Section—roadcut on State Highway 109, 2.5 km north of Eureka, St. Louis Co., MO (NW¼ NW¼ NE¼ Sec. 25, T 44 N, R 3 E; Eureka 7.5-minute Quad.). Deicke, Millbrig, and House Springs.
60. Mincke Hollow Section—exposure in south bluff of Meramec River along the St. Louis-San Francisco Railroad, 0.4 km southwest of Tyson, St. Louis Co., MO (near center E½ SE¼ SE¼ Sec. 21, T 44 N, R 4 E, Manchester 7.5-minute Quad.). Deicke (type section) and Millbrig; DRK-208, Kings Lake Formation, 2.3 m above Millbrig K-bentonite.
61. Eureka South Section—roadcut on west side of Bald Hill Road (State Route W) 2 km south of Eureka, St. Louis Co., MO (SW¼ SW¼ SE¼ irregular Sec. 1, T 43 N, R 3 E; Pacific 7.5-minute Quad.). Deicke, Millbrig, and House Springs.
62. House Springs Section—roadcut on east side of State Highway 30, 0.8 km north of intersection with highway W at House Springs, Jefferson Co., MO (irregular unnumbered section between Sec. 32 and Sec. 33, T 43 N, R 4 E; House Springs 7.5-minute Quad.). Deicke and Millbrig; DRK-245, Kings Lake Formation, 2.8 m above Millbrig K-bentonite; House Springs (type section).
63. Barnhart South Section—roadcut on Interstate Highway 55 (mile marker 183.1) 3.2 km south of I-55 bridge over Glaize Creek in Barnhart, Jefferson Co., MO (center N½ SW¼ NW¼ Sec. 6, T 41 N, R 6 E, Herculanum 7.5-minute Quad.). Deicke and Millbrig; DRK-271, Kings Lake Formation, 2.5 m above Millbrig K-bentonite; House Springs.
64. Bloomsdale Section—roadcut in southeast bluff of Establishment Creek where creek bends abruptly south then back north, 5 km northeast of Bloomsdale, Ste. Genevieve Co., MO (unnumbered section 0.5 km northwest of Sec. 5, T 38 N, R 8 E; Bloomsdale 7.5-minute Quad.). Deicke and Millbrig; DRK-266 and -267, Kings Lake Formation, 0.6 m and 1.4 m below Dunleith Formation; House Springs; and DRK-270, unnamed K-bentonite in the Platteville Group 0.6 m below Deicke.
65. Ste. Genevieve Southwest Section—quarry on Klein farm on southwest side of Interstate Highway 55, 3.2 km southeast of intersection of I-55 and State Highway 32, 7 km southwest of Ste. Genevieve, Ste. Genevieve Co., MO (southern part of irregular Sec. 7, T 37 N, R 9 E; Ste. Genevieve 7.5-minute Quad.). Millbrig; DRK-210, Kings Lake Formation, 0.3 m below Dunleith Formation.
66. Illmo Section—Grays Point quarry 3 km northeast of Illmo, Scott Co., MO (390 m east and 120 m north of the NE corner of Sec. 28, T 30 N, R 14 E; Thebes 7.5-minute Quad.). Deicke.
67. Le Mars, Iowa Core—Iowa Geological Survey Camp Quest core (depth 697.0 ft; elev. 1245 ft), 3 km northeast of Le Mars, Plymouth Co., IA (SW¼ Sec. 2, T 92 N, R 45 W; 42° 48'N, 96° 08'W; Le Mars 15-minute Quad.). Deicke sample DRK-211, upper part of Platteville Group.

